WO2004096301

Publication Title:

FLUID-ABSORBENT COMPOSITIONS AND ARTICLES, POROUS ARTICLES, AND METHODS FOR MAKING THE SAME

Abstract:

This invention provides, in several aspects, fluid-absorbent compositions and articles (such as films, sheets, fibers, foams, nonwovens, or molded articles), and methods for making the same, wherein small superabsorbent particles are incorporated into particular matrix-polymers. Upon contact with a fluid (such as water or saline), the particles exposed to the fluid swell and percolate out of the composition or article and expose other particles to the fluid. In another aspect, this invention provides elastic, porous articles (such as films or membranes) made from the above-described articles (using elastic matrix-polymers) by contacting that article with fluid to percolate at least a portion of the absorbent particles out of the article, thereby creating a plurality of pores in the residual elastic matrix-polymer. The articles of this invention are useful in many end-use applications, such as packaging, hygiene, construction, agriculture, membrane, medical, and other end-use applications.

Data supplied from the esp@cenet database - http://ep.espacenet.com

This Patent PDF Generated by Patent Fetcher(TM), a service of Patent Logistics, LLC

BEST AVAILABLE COPY

(19) World Intellectual Property Organization International Bureau



I COLI TUDICO DE CONTRETOR DE C

(43) International Publication Date 11 November 2004 (11.11.2004)

(10) International Publication Number WO 2004/096301 A2

(51) International Patent Classification7:

A61L 15/00

(21) International Application Number:

PCT/US2004/012435

(22) International Filing Date: 22 April 2004 (22.04.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/464,980

24 April 2003 (24.04.2003)

- (71) Applicant (for all designated States except US): DOW GLOBAL TECHNOLOGIES INC. [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ALLGEUER, Thomas, T. [AT/CH]; Felsenrainstrasse 7A, CH-8832 Wollerau (CH). CHANG, Andy, C. [US/US]; 504 Highway 332 #912, Lake Jackson, TX 77566 (US). HERSCHE, Emil, E. [CH/CH]; Im Höfli 15, CH-8832 Wollerau (CH). KIM, Young-Sam [KR/US]; 1812 Oakfield Drive, Midland, MI 48640 (US).
- (74) Agent: FARRELL, Daniel, R.; The Dow Chemical Company, Intellectual Property Section, P.O. Box 1967, Midland, MI 48674-1967 (US).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG):

Published:

without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FLUID-ABSORBENT COMPOSITIONS AND ARTICLES, POROUS ARTICLES, AND METHODS FOR MAKING THE SAME

(57) Abstract: This invention provides, in several aspects, fluid-absorbent compositions and articles (such as films, sheets, fibers, foams, nonwovens, or molded articles), and methods for making the same, wherein small superabsorbent particles are incorporated into particular matrix-polymers. Upon contact with a fluid (such as water or saline), the particles exposed to the fluid swell and percolate out of the composition or article and expose other particles to the fluid. In another aspect, this invention provides elastic, porous articles (such as films or membranes) made from the above-described articles (using elastic matrix-polymers) by contacting that article with fluid to percolate at least a portion of the absorbent particles out of the article, thereby creating a plurality of pores in the residual elastic matrix-polymer. The articles of this invention are useful in many end-use applications, such as packaging, hygiene, construction, agriculture, membrane, medical, and other end-use applications.

FLUID-ABSORBENT COMPOSITIONS AND ARTICLES, POROUS ARTICLES, AND METHODS FOR MAKING THE SAME

The present invention relates to fluid-absorbent compositions and articles, and methods for manufacturing the same. In another aspect, this invention relates to porous articles (such as porous films or membranes), and methods for making the same.

Superabsorbent polymers ("SAPs") are well-known materials that are used in a variety of applications, including water-barrier applications in the construction industry, and liquid absorbers in food-packaging systems, as well as in hygiene and medical applications. SAPs are known to absorb several times their weight of fluids, such as moisture, water, saline solution, and the like.

In some applications, one of the challenges of using SAP particles is the containment or fixation of those particles. Different approaches to contain or fix the SAP particles have been taken. In some applications a matt or batt is wrapped with a liner, and the matt or batt usually contains the SAP in particulate form, such as in USP 3,670,731. However, loss of particles and/or redistribution of the SAP particles within the matt or batt (sometimes referred to as shakeout) often occurs. A variety of attempts have been made to reduce shakeout. Embedding SAP particles into various thermoplastic polymers has also been proposed, such as in Japanese patent application JP 57-145151 A (published 1982); PCT publications WO 99/57201 and WO 02/07791; GB patent 2203985; and USP 4,806,598.

In power and communication cable applications, different approaches have been tried to bind or fix SAP for use as water-blocking agents. For examples, see US Patents 4,966,809, 5,461,195, and 5,925,461, as well as PCT publication WO 02/07791.

In the manufacturing of fibers, the use of mixtures of SAPs and binders have been proposed, such as in EP 0 425,269 A2 and US Patent 6,194,630.

Other methods to bind SAP are known, such as disclosed in US Patents 3,669,103, 3,926,891, 3,935,099, 3,997,484, 4,076,673, 4,090,013, 4,117,184, 4,392,908, and 5,516,585.

25

5

10

15

20

This invention provides a method for manufacturing a fluid-swellable non-molten mass, comprising the steps of:

- (a) providing a plurality of fluid-swellable absorbent particles;
- (b) incorporating those absorbent particles into at least one molten matrix-polymer to form a molten compound, which matrix-polymer (as measured in accordance with ASTM D638) has a 2 percent secant modulus of about 60 or less;
- (c) processing that molten compound to form at least one molten or semi-molten mass having an external surface;
- (d) applying an inorganic powder onto at least a portion of the external surface of the molten or semi-molten mass; and
- (e) cooling the molten or semi-molten mass with a cooling medium that is substantially free of any fluid that would swell the absorbent particles, so as to form a non-molten mass.

This invention also provides a composition of matter comprising:

5

10

15

20

25

30

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those absorbent particles being sufficiently small to pass through a 150-micron sieve; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which those absorbent particles are at least partially embedded so as to initially constrain those absorbent particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those absorbent particles from the matrix-polymer when those absorbent particles are swollen by contact with fluid, which composition (when tested in the SAP-Utilization Test) has a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.

This invention further provides a composition of matter comprising:

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those particles being sufficiently small to pass through a screen with openings of 150 microns; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which the absorbent particles are at least partially embedded to form an interconnected network of those particles within the matrix-polymer so as to initially

constrain the particles but, upon contact with a fluid that swells those particles, permit the release of fluid-swellen absorbent particles from the matrix-polymer and exposure of other absorbent particles that are interconnected with the released particles,

wherein the composition is substantially free of polar compounds or any polymer having a polar-functional group or other functional group that interacts ionically or covalently with the absorbent particles.

In another embodiment this invention provides an article having a thickness, comprising:

10

15

20

25

30

(a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those particles being sufficiently small to pass through a screen with openings of 150 microns; and

(b) between 30 and 80 weight percent of at least one matrix-polymer in which the absorbent particles are at least partially embedded to form an interconnected network of those particles within the matrix-polymer so as to initially constrain the particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those fluid-swollen absorbent particles from the matrix-polymer and exposure of other absorbent particles that are interconnected with the released particles, and

(c) 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and

wherein the article is substantially free of polar compounds or any polymer having a polarfunctional group or other functional group that interacts ionically or covalently with the absorbent particles.

In yet another embodiment this invention provides an article having a thickness, comprising:

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those absorbent particles being sufficiently small to pass through a 150-micron sieve; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which those absorbent particles are at least partially embedded so as to initially

constrain those absorbent particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those absorbent particles from the matrix-polymer when those absorbent particles are swollen by contact with fluid, and

5

10

15

20.

25

30

(c) 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and which components (a), (b) and (c), when tested in the SAP-Utilization Test, have a

Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-

Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.

The articles of the present invention may be employed in a wide variety of uses as are known in the art, such as, for example, the assembly or construction of water-barrier systems for the construction industry, porous membranes, active-packaging systems, liquid collection of draining food-stuff, protective covers to keep surfaces dry, fire-protection covers, water or humidity extraction from the atmosphere, soils sealants, water storage in soils or around plants, mulch films with controlled release pesticides, ink absorbent, and various disposable absorbent articles, such as sanitary napkins, disposable diapers, hospital gowns, medical wraps or bandages, bed pads, and the like.

In still another embodiment, this invention provides an elastic, micro-porous film or membrane and a method for making that film or membrane, by contacting a non-molten, SAP-containing elastic film or sheet (made in accordance with the above methods, compositions, or articles) with a fluid (for example, deionized water or saline) that causes a portion of the absorbent particles to percolate out of the film or sheet, thereby leaving an elastic, porous film or membrane. The elastic films or membranes of this invention may be used in a wide variety of uses as known in the art, such as, for example, filtration of fluid/solid systems, fluid separations, water separation or purification, packaging, environmental processes, smart membranes, and the like.

Description of the Drawings

Fig. 1 is a diagram showing how film samples are prepared for surface and cross-sectional analysis by Scanning Electron Microscopy (SEM) to determine the presence of interconnected networks of SAP particles in a matrix-polymer.

Fig. 2 is a SEM micrograph showing an interconnected network of SAP particles in a cross-section of a film formed in accordance with this invention.

Figs. 3A, 3B, and 3C are SEM micrographs showing various cavities or pores formed at the surface of a porous film formed in accordance with this invention.

5

10

Figs. 4A and 4B are SEM micrographs showing the cross-sections of two test specimens cut from separate portions of the same film formed in accordance with this invention. The film was divided into two portions — a control portion and a portion that was washed with deionized water. Fig. 4A shows a machine-direction cross-section of a test specimen cut from the control film sample (that is, that has not been contacted with water), and Fig. 4B shows a machine-direction cross-section of a test specimen cut from the washed film sample.

Figs. 5A and 5B are SEM micrographs showing, in Fig. 5A, the surface of a porous film of this invention as compared to, in Fig. 5B, the surface of a comparative film.

15

20

25

30

Definitions

As used in this patent application, the following capitalized terms have the following meanings:

"2 percent Secant Modulus," as used to characterize a candidate matrix-polymer or blend of matrix-polymers, means the secant modulus (expressed in Mega-Pascals [MPa]) of that candidate at 2 percent strain, as measured by ASTM-D638-01 (see in particular paragraph 11.5, and the "toe compensation" in Annex A1), with the samples to be measured being prepared either in accordance with ASTM-D638-01 or (for smaller samples) in accordance with the micro-tensile geometry described in ASTM D1708-96, the teachings of which are incorporated by reference herein.

"A Factor," or "Max-SAP-Utilization Factor," as used to describe the components (that is, the SAP(s), the matrix-polymer(s), surfactant(s), and possibly other components) of an article or composition, means the maximum percentage of that SAP that is released from (or percolated out of) a standard film sample made from those components over a standard period of time, when tested in accordance with the SAP-Utilization Test described in this patent application.

"Adhesion Factor," as used to characterize the suitability of the various combinations of components (other than SAP) of a composition for use in this invention, is a measure of the adhesion between that combination and the SAP particles in question. A combination of components has a "low Adhesion Factor" if the addition of the SAP particles to the other components results in a decreased engineering stress response at engineering strains higher than 100 percent, as compared to the other components alone; and conversely, a combination has a "high Adhesion Factor" if the addition of the SAP particles results in an increased engineering stress at engineering strains higher than 100 percent, as compared to the other components alone.

"B Factor," or "SAP-Utilization Rate," as used to describe the components (that is, the SAP(s), the matrix-polymer(s), surfactant(s), and possibly other components) of an article or composition, is a measure (in minutes⁻¹) of the rate at which that SAP is released from (or percolated out of) a standard film sample made from those components, when tested in accordance with the SAP-Utilization Test described in this patent application.

10

15

20

25

30

"Bicomponent fiber" means a fiber that has two or more distinct polymer regions or domains. Bicomponent fibers are also sometimes known as conjugated or multi-component fibers. The polymers are usually different from each other although two or more of the components may comprise the same polymer. The polymers are arranged in substantially distinct zones across the cross-section of the bicomponent fiber, and usually extend continuously along the length of the bicomponent fiber. The configuration of a bicomponent fiber can be, for example, a sheath/core arrangement (in which one polymer is surrounded by another), a side-by-side arrangement, a pie arrangement or an "islands-in-the sea" arrangement. Bicomponent fibers are further described in USP 6,225,243, 6,140,442, 5,382,400, 5,336,552 and 5,108,820.

"Elastic" means that the article in question (for example, a fiber or film) is capable of returning essentially to its original unstretched length after repeatedly (up to four times) being subjected to a strain that stretches that article to double its unstretched length (that is, 100 percent strain). Elasticity or lack of elasticity can also be described in terms of the "permanent set" of the article. Permanent set represents the degree of lack (or loss) of elasticity in the article. As an article is stretched to a certain length and subsequently released to allow it to recover toward its original lengthy, the permanent set of that article is a measure of the degree to which that article (after one or more cycles) fails to return to its

original length. "Elastic materials" are also sometimes referred to in the art as "elastomers" or as being "elastomeric."

"Extractables," as used to describe SAP, means the water-soluble-polymer content of that SAP, as determined by the Extractables Test Method described in this patent application.

5

10

15

20

25

30

"Fluid-swellable," as used to describe an object, means that the object becomes larger in size as it absorbs a particular fluid. SAPs are examples of fluid-swellable objects. As SAPs absorb water, saline solution, or other absorbable liquid, the SAP swells to many times its original (that is, dry) size. As used to describe the articles or compositions of this invention, the article or composition is considered "fluid-swellable" if it contains one or more components (for example, the SAP particles) that are "fluid-swellable."

"Interconnected," as used to describe two or more SAP particles in relationship to one another, means that the SAP particles are positioned so as to be in fluid communication with each other. This may mean that the particles are in physical contact with each other such that fluid can flow from one particle directly into another; or that there is a gap or other fluid passageway between those particles. Typically, an interconnected network will have some SAP particles in direct physical contact with other particles, and other SAP particles that are not physically contacting each other, but that are interconnected with one or more other SAP particles by a gap or other fluid passageway in the surrounding matrix.

"Interconnected Network," as used to describe SAP-particles dispersed inside a compound or article means that a significant percentage of those particles are "interconnected" such that when a fluid contacts SAP-particles exposed on an external surface of that compound or article, that fluid is absorbed, with consequent SAP-particle swelling, not only by the external-surface-exposed SAP-particles, but also SAP-particles that, at least initially, are not directly exposed to the external surface.

"Melt Flow Rate" or "MFR," as used to describe a matrix-polymer, means the melt flow rate, expressed in grams per 10 minutes, as measured in accordance with ASTM D-1238. For ethylene-based interpolymers, the MFR is measured under conditions of 190° C. and total load of 2.16 kg. (formerly known as "Condition E"). For propylene-based interpolymers, the MFR is measured under conditions of 230° C. and total load of 2.16 kg. (formerly known as "Condition L").

"Modified Centrifuge Capacity," or "mCC," as used to describe SAP, means the capacity of the SAP particles per se (that is, separate from any matrix-polymer) to absorb a 0.9 weight percent sodium chloride solution, as determined by the modified centrifuge capacity test method described in this patent application.

5

15

20

25

30

"Molten," as used with respect to a polymer, means that the polymer is substantially completely in a fluid state, rather than a rigid vitreous state, such as occurs when a crystalline or a semi-crystalline polymer is heated to above its melting point or an amorphous polymer is heated to above its glass-transition temperature (Tg). "Semi-molten" means that a large portion of the polymer is in a fluid state, even though lesser (usually the high molecular fraction of the polymer) portions remain in a solid state, such as occurs when a semi-crystalline polymer having a broad molecular weight distribution is heated to temperatures slightly above the melting point of the crystalline portions, or a lightly crosslinked amorphous polymer is heated to temperatures just above the glass-transition temperature. "Non-molten" means that the polymer is in a solid state, such as occurs when a crystalline or a semi-crystalline polymer is solidified below its melting point, or an amorphous polymer is solidified below its glass-transition temperature.

"Nonelastic material" means a material, for example, a fiber or film, that is not elastic as defined above.

"Nonwoven" means a web or fabric having a structure of individual fibers or threads which are randomly interlaid, but not in an systematic order as is the case of a knitted fabric. The compositions of the present invention can be employed to prepare nonwoven structures as well as composite structures of elastic nonwoven fabric in combination with nonelastic materials.

"Percolate" is used in this patent application not only in the normal sense of a fluid passing through a porous network (for example, water vapor passing through the pores of the porous membranes of this invention), but also to describe that activity by which SAP particles (that initially are fully or partially embedded in the matrix-polymer of an article) will swell and be released (or escape) from that matrix-polymer. So when we describe the SAP particles as "percolating" out of the article, we mean that the SAP particle swells into a gel and that gel escapes from the matrix-polymer that initially constrained the SAP particle.

"Polymer" means a macromolecular compound prepared by polymerizing monomers of the same or different type. "Polymer" includes homopolymers, copolymers,

terpolymers, interpolymers, and so on. The term "interpolymer" means a polymer prepared by the polymerization of at least two types of monomers or comonomers. "Interpolymer" includes, but is not limited to, copolymers (which usually refers to polymers prepared from two different monomers or comonomers, but is also used in a broader sense as a synonym for an interpolymer with two or more monomers or comonomers), terpolymers (which usually refers to polymers prepared from three different types of monomers or comonomers), tetrapolymers (which usually refers to polymers prepared from four different types of monomers or comonomers), and the like. The term "monomer" or "comonomer" refers to any compound with a polymerizable moiety which is added to a reactor in order to produce a polymer.

5

10

15

20

25

30

"Partially coat," as used with respect to the application of inorganic powder to the external surface of the molten or semi-molten mass (comprising the SAP particles and matrix-polymer) formed in the method of this invention, means that the powder adheres to portions of that surface so as to reduce the tendency of that surface to adhere (for example, stick by the inherent tackiness of the mass in question) to either itself (other particles of the same molten mass such as pellets) or to other surfaces (for example, equipment, or other masses). Depending upon the tackiness of the mass in question, it may be necessary to adhere the powder to a very high percentage (for example, about 80 percent or more, where the mass is very tacky) of that surface, or to a very low percentage (for example, about 30 percent or less, where the mass is less tacky) of that surface.

"Particle Size," as used with respect to the SAP particles, is defined as the dimension determined by sieve size analysis. Thus, for example, a particle that is retained on a U.S.A. Standard Testing Sieve with 710 micron openings (for example, No. 25 U.S. Series Alternate Sieve Designation) is considered to have a size greater than 710 microns; a particle that passes through a sieve with 710 micron openings and is retained on a sieve with 500 micron openings (for example, No. 35 U.S. Series Alternate Sieve Designation) is considered to have a particle size between 500 and 710 microns; and a particle that passes through a sieve with 500 micron openings is considered to have a size less than 500.

"Powder," as used with respect to the inorganic powder used in the method of this invention, means finely divided particles that are very small relative to the dimensions of the surface to which the powder is applied. Typically, the inorganic powders used in the method of this invention will have a particle size sufficient to pass through a sieve having

openings of 10 microns or less.

"Substantially Free," as used with respect to the concentration of a particular component in a composition or article, means that the composition or article contains so little of that component that the component does not affect negatively the performance or properties of that composition or article (in the sense that the fluid-absorbency of the composition or article is impeded). As an example, if a component only begins impacting the performance or properties of an article negatively at a concentration of 1 weight percent, an article having less than 1 weight percent of that component would be "substantially free" of that component.

10

15.

20

25

5

Test Methods

The following test methods are used in this patent application to describe certain properties of various components or articles.

1. Extractables Test Method

The following test method is used to determine the amount of water-soluble polymer ("extractables") contained in particular SAP particles, after 16 hours extraction with saline.

One gram of the SAP particles to be analyzed and 185 grams of 0.9 weight percent sodium chloride solution are placed in a 250 mL jar which is then capped and put on a shaker (125 rpm) for 16 hours. A portion of the extract (that is, the aqueous solution which now contains water-soluble polymers) is filtered to remove gels by setting up a filtering flask with a Buchner funnel and Whatman filter paper GF/F having a diameter of 11 cm, to generate a filtrate. Using a Metrohm 670 Titoprocessor with sample changer 673, the pH of a 30 grams sample of that filtrate is adjusted to pH 10 by adding a 0.1 N solution of NaOH. The resulting pH-adjusted filtrate is then titrated to pH 2.7 by adding a 0.1 N solution of hydrochloric acid. A similar titration is made on a control saline solution (that is, that has not contacted any SAP).

The amount of water-soluble polymer (percent extractables) of the SAP being tested is then calculated as follows:

where:

5

10

15

20

Va = volume of titrant needed to titrate filtrate (mL)

Vb = volume of titrant needed to titrate blank (mL)

N = normality of the titrant (mol/L)

Mw = the equivalent molecular weight of SAP

185 = total amount of solution (g)

Ws = weight of sample (for example, 1.0 g)

Wf = weight of filtrate (for example, 30.0 g)

2. mCC Test Method

Since the SAP particles useful in this invention are so finely-divided, it is difficult to obtain accurate data using typical centrifuge capacity methods. For this patent application, as a measure of the water-absorption capacity of the SAP particles, the following modified centrifuge capacity (mCC) test method is used:

A sample $(0.200 \pm 0.005 \text{ grams})$ of the SAP particles is weighed (W_1) and then poured into a first teabag (standard size, 4 cm by 4 cm) and that first teabag is heat sealed. That first heat-sealed teabag is then placed into a second, larger teabag (7.6 cm by 6.4 cm) which is then also heat-sealed. An otherwise identical blank (that is, containing no SAP) teabag-in-teabag control is also prepared.

The teabag-in-teabag control and the teabag-in-teabag containing SAP are both immersed in a 0.9 wt percent NaCl solution. After 120 min, both are removed from the saline solution and placed into a centrifuge basket, and then centrifuged for three minutes at 1500 rpm. The teabag-in-teabag control and the teabag-in-teabag sample containing the SAP are then each removed and weighed. From that data, the mCC is calculated as follows:

25
$$mCC = \frac{(w_2 - w_3) - w_1}{w_1} (g/g)$$

 $w_1 = dry SAP$ fines weight

w₂ = centrifuged teabag-in-teabag containing SAP

w₃ = centrifuged control teabag-in-teabag

30

3. SAP-Utilization Test Method

5

10

15

20

25

30

As a measure of the suitability of particular combinations of components (that is, the SAP particles, matrix-polymers, and other components) for use in this invention, a test method was devised to determine both the initial rate of SAP utilization ("SAP-Utilization Rate" or "B Factor") and the percentage of SAP actually used ("Max-SAP-Utilization Factor" or "A Factor") in a standard film sample made from those components. The standard film samples are approximately 200 micron-thick films prepared by the compounding and roll-mill-fabricating method described in Examples 1 through 10 of this invention. The SAP-Utilization Test is conducted on those standard films as follows:

The components (that is, the SAP particles, matrix-polymer(s), surfactants, and other components) to be tested are intimately and uniformly compounded and processed (as described for the films made in Examples 1 through 10) into a film having a thickness of 200 microns, under conditions that avoid swelling of the SAP particles. Representative samples (each measuring 2.5 cm by 2.5 cm) are cut from the film to form 18 test specimens from each film to be tested. Each specimen is weighed (weight_{original}) and then attached to a wire-hanger designed to suspend the specimen in a beaker containing 500 mL of deionized water. Under conditions of about 50 percent relative humidity and about 20° C., at specified intervals of 1, 3, 10, 30, 100, and 180 minutes after the test specimens are immersed, three of the test specimens are removed and then evaluated to determine the percentage of the SAP originally present in that specimen that had percolated out of the test specimen. The evaluation involves gently scraping the gel (that is, formed by the percolated SAP plus the absorbed water) from the surface of the specimen, drying the remaining film test specimen (in a vacuum oven at 50° C.) to remove any residual water, and then weighing that dried film test specimen (weight_{time}), where "time" means the time of immersion (that is, 1 or 3 or 10 or 30 or 100 or 180 minutes) for that specimen. The SAP utilized for that test specimen is calculated as follows:

$$SAP \ utilization_{time} = \frac{\text{weight}_{\text{original}} - \text{weight}_{\text{time}}}{\text{weight}_{\text{original}}} \times 100\%$$
(I)

wherein "SAP utilization_{time}" is the percentage of original SAP that was percolated from the test specimen by that given time of immersion.

The SAP-utilization data from the test specimens using deionized water are then fitted to the following empirical equation, in order to determine the A Factor and B Factor for that combination of components:

$$SAP \ utilization_{time} = Ax(1-10^{-Bxtime}) \quad (II)$$

wherein "A" is the "A Factor" or "Max-SAP-Utilization Factor," and "B" is the "B Factor" or "SAP-Utilization-Rate Factor."

The B Factor is indicative of the slope of the initial rise in SAP utilization. The A Factor is indicative of the plateau in the curve as SAP utilization reaches a maximum.

The same test procedure may be run with a 0.9 weight percent solution of NaCl; however, the resulting SAP-utilization data will be somewhat different. If the data from the tests run with saline solution are fitted into the above equation, typically a somewhat lower A Factor will result as compared to that calculated from data from tests run with deionized water. In this patent application, the A Factor and B Factor used are from testing in deionized water, unless clearly indicated otherwise.

3. WVTR Test Method

5

10

15

20

25

. 30

The water-vapor-transmission rate ("WVTR") of a film, sheet, or membrane can be measured using known test methods and equipment, for example using the methods described in ASTM E 398-83 or ASTM E 96-00 or ISO/CD 15106, or using commercially available automatic equipment suitable for water vapor transmission rate testing, such as automatic water vapor permeability testers supplied by LYSSY AG, Zollikon, Switzerland (for example testers of LYSSY's L80 series, such as L80-4000 or L80-5000), or by MOCON in Minneapolis, Minnesota (for example a PERMATRAN 100K tester). The WVTR values and ranges set forth in this patent application are based on measurements performed using a LYSSY L80-4000J tester following the supplier's instructions and using the supplied GoreTex® membrane as the standard.

Description of Fluid-Absorbing Particles

The fluid-absorbing polymer particles useful in this invention are those that absorb many times their own weight of the fluid in question, such as water or aqueous liquids.

Called "superabsorbent polymers" or SAPs, those particles swell when they absorb the fluid.

5

10

. 15

20

25

30

The fluid-absorbing polymers can be any of the known hydrophilic polymers that are cross-linked and capable of absorbing large quantities of fluids causing the particle to swell to many times its dry size. These polymers are well known in the art and are widely commercially available.

Examples of some suitable SAPs and processes (including gel polymerization processes) for preparing SAPs are disclosed in USP 3,669,103; 3,670,731; 3,926,891; 3,935,099; 3,997,484; 4,076,663; 4,090,013; 4,093,776; 4,190,562; 4,286,082; 4,340,706; 4,446,261; 4,459,396; 4,654,039; 4,683,274; 4,708,997; 4,857,610; 4,985,518; and 5,145,906, the teachings of which are incorporated herein by reference. In addition, see Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998) and Lisa Brannon-Peppas and Ronald S. Harland, "Absorbent Polymer Technology" Elsevier (1990), the teachings of which are incorporated herein by reference.

Preferred SAPs are prepared from water-soluble α,β-ethylenically unsaturated monomers, such as monocarboxylic acids, vinyl polycarboxylic acids, acrylamide, and their derivatives. More preferred SAP are cellulosic or starch-graft copolymers, such as starch-g-poly(acrylonitrile), starch-g-poly(acrylic acid) and the like; polyacrylamides; polyvinyl alcohols; poly(acrylic acids); high-molecular-weight polymers, preferably cross-linked, of ethylene-oxide (EO) and propylene-oxide (PO); copolymers of sulfonic-acid-group-containing monomers, such as vinyl sulfonic acid, sodium sulfoethyl methacrylate, 2-Acrylamido-2-Methylpropane-sulfonic acid or the sodium salt (AMPS), and the like.

Most preferred SAPs are crosslinked, partially neutralized, and/or surface treated. Preferably, the level of crosslinking is selected to give the desired swelling characteristics for the particular application. Generally, the degree of neutralization is from 30 to 100 percent, more preferably from 50 to 80 percent. Neutralization with a basic substance containing a Group I metal ion, such as sodium, is preferred. A preferred surface treatment consists of a post-polymerization reaction to effect the surface crosslinking of the SAP.

Suitable SAPs include those marketed by The Dow Chemical Company under the trademark "DRYTECH," such as DRYTECH S100R and S230R, and those marketed by BASF under the trademark "Hysorb," and those marketed by Stockhausen under the trademark "CABLOC," provided in each case that any SAPs particles are too large (that is,

that do not pass through a sieve with the desired size openings) are removed or re-sized (for example, by milling or other grinding) to be within the desired size range.

Modified Centrifuge Capacity of SAP

5

10

15

20

25

30

For this invention, surprisingly, we have found that there are advantages to using SAPs that have moderate mCC values (as measured by the modified Centrifuge Capacity Test), as opposed to very high mCC values. Preferably, the SAPs used in the present invention will have an mCC (as measured in 0.9 wt. percent NaCl solution) that is less than about 60 g/g, and more preferably less than about 50 g/g, and most preferably less than about 40 g/g. The SAPs used in the present invention will have an mCC (as measured in 0.9 wt. percent NaCl solution) that is greater than about 10 g/g, more preferably greater than about 20 g/g, and most preferably greater than about 30 g/g.

Extractables Content of SAP Particles

For this invention, we prefer to use SAP particles that have a relatively low extractables content. As measured by the Extractables Test, the SAP particles preferably have an extractables content less than 40, more preferably less than 30, and most preferably less than 20 percent by weight of the dry SAP. If the available SAP particles do not have the desired extractables content, their extractables content should be adjusted into the desired range by subjecting the SAP to one or more of the heat-treating, surface crosslinking, and/or ionic crosslinking methods known in the industry.

For a given matrix-polymer and a given ratio of the SAP-particle size to the article thickness, we found surprisingly that use of SAP particles having lower mCC and lower extractables (that is, within the preferred ranges described above) actually result in a higher Utilization Rate (the B Factor) in the article, when compared to otherwise identical articles made with SAP particles having a higher mCC and higher extractables content (that is, outside the preferred ranges described above).

Pre-treatment of SAP

In the gel polymerization of water-swellable polymers, monomers are polymerized in aqueous solution. Certain additives, such as crosslinking agents, are incorporated into the monomer mixture. The product of the polymerization process is

typically dried and subjected to mechanical means of particle-size reduction and classification (including chopping, grinding, and sieving) in order to provide SAP particles meeting the desired properties. If desired, the dried SAP particles may be further surface-modified (for example, by surface crosslinking or ionic crosslinking) and/or heat-treated, such as disclosed in US Patent 6,323,252, the teachings of which are incorporated by reference herein. Further, if the available SAP-particles do not have the desired properties (for example, the particle size, mCC, and/or extractables content described herein), SAP-particles having the desired properties usually can be prepared from those available SAP-particles by appropriate treatment (for example, milling, screening, and/or subjecting the SAP to one or more of the heat-treating, surface crosslinking, and/or ionic crosslinking methods known in the industry) before incorporation into the matrix-polymer.

Quantity of SAP

5

10

15

20

25

30

The amount of the SAP to be included according to the present invention will vary depending, for example, upon the type of SAP used, the type of matrix-polymer used, the dimensions of the article relative to the size of the SAP particles, the article's end-use application, the desired SAP-Utilization Rate, and the desired Max-SAP-Utilization Factor.

If the concentration of SAP particles in the matrix-polymer is too low, the SAP-Utilization Rate and Max-SAP-Utilization Factor may be very low. Although we do not desire to be limited by any theory of operation, we envision that, for any given combination of components and article configuration, a certain minimum SAP-particle concentration is needed to form an interconnected network of SAP particles that enables a higher SAP-Utilization Rate and/or Max-SAP Utilization Factor. Above that minimum concentration, more extensive interconnected networks are formed, which should result in some further increase in the SAP-Utilization Rate and Max-SAP Utilization Factor.

On the other hand, if the concentration of SAP particles is too high, the compound tends to be more difficult to process into the desired articles and (at very high concentrations) the residual integrity of the article (that is, the matrix-polymer and any SAP particles remaining in the article after percolation of the swollen SAP particles out of the article) may not be satisfactory.

For the present invention, depending upon the end-use application, the SAP is present in an amount of about 20 weight percent or more, preferably about 25 weight

percent or more, more preferably about 30 weight percent or more, even more preferably about 35 weight percent or more, and most preferably about 40 weight percent or more, in each case based on the dry weight of the total compound (that is, the SAP, plus matrix-polymer). Depending upon the end-use application, the amount of SAP polymer is present in an amount of about 70 weight percent or less, preferably about 65 weight percent or less, more preferably about 60 weight percent or less, even more preferably about 55 weight percent or less, and most preferably about 50 weight percent or less, in each case based on the dry weight of the total compound (that is, the SAP, plus matrix-polymer).

10 <u>Composition of Matrix-Polymers</u>

15

20

25

30

A variety of matrix-polymers are useful in the present invention, including both single-component polymers or multi-component blends of similar or different polymers. A variety of candidate matrix-polymers should meet the parameters specified in this patent application.

Suitable polyolefin-based matrix-polymers include certain plastomeric or elastic copolymers of ethylene and/or propylene with one or more unsaturated comonomers (such as C₄-C₂₀ alpha-olefins, C₄-C₂₀ dienes or polyenes, styrenic compounds, and the like), including ethylene-propylene rubber (EPR) and ethylene-propylene-diene (EPDM). Other suitable elastic polymers include certain styrene-block copolymers (for example, SBS, SIS), and hydrogenated styrene-block copolymers (for example, SEBS).

Among the propylene-based copolymers, suitable matrix-polymers include certain plastomeric or elastic copolymers made from at least about 60 weight percent propylene monomer, and from 0.1 to 35 weight percent of ethylene monomer, and from 0 to 35 weight percent of one or more unsaturated comonomers, provided that the combined content of ethylene and the unsaturated comonomer(s) does not exceed about 40 weight percent. Elastic propylene-based copolymers are preferred.

Potentially useful elastic propylene-based copolymers are disclosed in EP1003814B1, and US Patents 4,971,936; 5,089,573; 5,118,649; 5,118,767; 5,118,768; 5,134,209; 5,164,352; 5,229,477; 5,270,276; 5,270,410; 5,294,581;6,525,157 and 6,268,063, the teachings of which are incorporated by reference herein.

The elastic propylene-based copolymers described in co-pending patent application U.S. serial number 10/139,786, filed on May 5, 2002, are particularly preferred, the

teachings of which patent application are incorporated by reference herein. Those are copolymers of propylene, ethylene and, optionally, one or more unsaturated comonomers, for example, C₄₋₂₀ alpha-olefins, C₄₋₂₀ dienes, styrenic compounds, etc. These copolymers are characterized as comprising at least about 60 weight percent (wt percent) of units derived from propylene, about 0.1-35 wt percent of units derived from ethylene, and 0 to about 35 wt percent of units derived from one or more unsaturated comonomers, with the proviso that the combined weight percent of units derived from ethylene and the unsaturated comonomer does not exceed about 40. These copolymers are also characterized as having (i) a Melt Flow Rate (MFR, ASTM D-1238, 230° C./2.16 kg.) between 0.01 and 1,000, (ii) a narrow MWD, that is, less than about 3, (iii) ¹³C NMR peaks corresponding to a regio-error at 14.6 and 15.7 ppm, the peaks of about equal intensity and representing 0.02 to 7 mole percent of the propylene insertions, and (iv) a Bvalue greater than about 1.3. These copolymers are further characterized in that the propylene sequences are substantially isotactic, that is, they have an isotactic triad (mm) measured by ¹³C NMR of greater than about 0.85. "Substantially isotactic propylene sequences" and similar terms mean that the sequences have an isotactic triad (mm) measured by ¹³C NMR of greater than about 0.85, preferably greater than about 0.90, more preferably greater than about 0.92 and most preferably greater than about 0.95. Isotactic triads are described in, for example, USP 5,504,172 and WO 00/01745 and refer to the isotactic sequence in terms of a triad unit in the copolymer molecular chain determined by ¹³C NMR spectra. NMR spectra are determined as described in copending US patent application US Serial number 10/139,786, filed on May 5, 2002.

10

15

20

25

30

Highly preferred for use as a propylene-based copolymer for the matrix-polymer are those elastic propylene-based copolymers (described in U.S. serial number 10/139,786) comprising from 8 to 20 weight percent of units derived from ethylene, with the balance being units derived from propylene. More preferably, those propylene-based copolymers comprise from 10 to 17, most preferably from 12 to 16, percent of units derived from ethylene.

Among the ethylene-based copolymers, suitable matrix-polymers include certain plastomeric or elastic copolymers made from at least about 55 weight percent ethylene monomer, with the remainder being from 3 to 45 weight percent of one or more unsaturated comonomers (such as C₃-C₂₀ alpha-olefins, C₄-C₂₀ dienes or polyenes, styrenic

compounds, and the like). Elastic ethylene-based copolymers are preferred. Among those preferred elastic ethylene-based copolymers are:

(1) the elastic, homogeneous, substantially linear (that is, having long chain branching levels of 0.01 - 3 long chain branches per 1000 carbons, and a very narrow molecular weight distribution) ethylene-based polymers as described in US Patents 5,272,236, 5,278,272, and 5,665,800, and in particular those having a density of 0.885 gm/cm³ or less, more preferably those having a density of 0.875 gm/cm³ or less, and most preferably those having a density of 0.865 gm/cm³ or less. Suitable matrix-polymers of this type are available from The Dow Chemical Company under the trademark "AFFINITY."

5

10

15

25

30

- the elastic, homogeneous, linear (that is, having a very narrow molecular weight distribution, but essentially less than 0.01 long chain branches per 1000 carbons) ethylene-based polymers as described in US Patents 3,645,992, 5,026,798, and 5,055,438, and in particular those having a density of 0.885 gm/cm³ or less, more preferably those having a density of 0.875 gm/cm³ or less, and most preferably those having a density of 0.865 gm/cm³ or less. Suitable matrix-polymers of this type may be available from ExxonMobil Chemical Company under the trademark "Exact," or from Mitsui Chemical Company under the trademark "Tafmer."
- (3) the elastic, substantially random interpolymers of ethylene with a vinylidene aromatic comonomer (such as styrene), and optionally a C₃ to C₂₀ alpha-olefin comonomer, as described in US Patent 6,190,768, and in particular those elastic, substantially random interpolymers of ethylene, styrene, and optionally propylene, having 25 to 45 weight percent of styrene-monomer units.

The teachings of the cited US Patents are hereby incorporated by reference in their entirety.

If desired, the matrix-polymer may be a blend of two or more polymers. For example, the above-described homogeneous, substantially linear ethylene copolymer may be blended advantageously with other polyethylenes of various densities (such as low density polyethylene (LDPE), or with ethylene-based copolymers) that do not, per se, meet the preferred parameters for the matrix-polymer, provided that the blend does meet those parameters. Similarly, blends of elastic ethylene-based or propylene-based copolymers with isotactic polypropylene homopolymer, high crystallinity polypropylene (HCPP), impact copolymers of propylene, and/or random copolymers of propylene may be suitable for use as

the matrix-polymer. Elastic blends of ethylene-based or propylene-based interpolymers with other non-polar polymers (such as styrene-block-copolymers, or hydrogenated styrene-block-copolymers) may also be suitable.

5 Melt Flow Rate of the Matrix-Polymer

10

15

20

25

30

In a few of the end-use applications for the present invention (such as melt-blown fibers), it is desired that the matrix-polymer have a high Melt Flow Rate, such as from 500 to 1500 gm/10 minutes. However, for most of the other end-use applications, it is desired that the matrix-polymer (either a single polymer or blend of polymers) have a relatively low Melt Flow Rate (MFR). For ethylene-based matrix-polymers it is preferred that the MFR (ASTM D-1238-00, 190° C./2.16 kg.) be less than about 50 gm/10 minutes, more preferably less than about 30 gm/10 minutes, even more preferably less than about 10 gm/10 minutes, and most preferably in the range of 0.1 to 5 gm/10 minutes. For propylene-based matrix-polymers, it is preferred that the MFR (ASTM D-1238-00, 230° C./2.16 kg.) be less than about 100 gm/10 minutes, more preferably less than about 50 gm/10 minutes, even more preferably less than about 40 gm/10 minutes, and most preferably in the range of 1 to 30 gm/10 minutes.

Quantity of Matrix-Polymer

It is desired that the matrix-polymer (that is, a single polymer or blend of polymers) is present in a quantity sufficient for the matrix-polymer to form a continuous phase in the compound or article in question. Where the SAP-containing matrix-polymer constitutes a component of a multi-component system (such as a film, foam, or nonwoven layer on a substrate), the matrix-polymer should form a continuous phase in that component. For the present invention, the matrix-polymer is present in an amount of about 30 weight percent or more, preferably about 35 weight percent or more, more preferably about 40 weight percent or more, even more preferably about 45 weight percent or more, in each case based on the dry weight of the total compound (that is, the SAP, plus matrix-polymer). The matrix-polymer is present in an amount of about 80 weight percent or less, preferably about 70 weight percent or less, more preferably about 65 weight percent or less, even more preferably about 60 weight percent or less, and most preferably about 55 weight percent or

less, in each case based on the dry weight of the total compound (that is, the SAP, plus matrix-polymer).

2 percent Secant Modulus of the Matrix-Polymer

We have discovered that the modulus of the matrix-polymer or matrix-polymer blend has a significant influence on the SAP-Utilization Rate, that is, the rate at which the swelling SAP particles release (or percolate) from the article to expose other SAP particles interconnected with those exposed to the fluid. Matrix-polymers having a relatively low modulus tend to release the swelling SAP more rapidly than higher modulus polymers.
Accordingly, in order to increase the SAP-Utilization Rate, it is desired to use matrix-polymers or blends having a 2 percent Secant Modulus of 60 MPa or less, preferably 50 MPa or less, more preferably 40 MPa or less, and most preferably 30 MPa or less. However, we also envision that there may be a benefit in selecting as a matrix-polymer a single polymer or blend of polymers that has a somewhat higher modulus so that the matrix-polymer will somewhat restrict (or retard) the release of the SAP, in order to achieve a slower SAP-Utilization Rate in those end-use applications where a slower rate is desired.

Interaction Between Matrix-Polymer and SAP Particles

20

25

30

We have discovered that it is also desirable that the compound formed contain little or no polar groups or compounds, and little or no other compounds that have a functional group that interacts ionically or covalently with the SAP particles. This means that matrix-polymer, and any other non-SAP components present in significant quantity in the compound, should be non-polar and not have those functional groups. By way of example, the compounds and articles of the present invention should contain no significant quantity of those polar diluents or polar copolymers disclosed in US Patent 6,534,572, or those thermoplastic resins disclosed in US patent application publication 2002/0039869 as having functional groups (for example, carbonyl or acyl groups) that interacts with the SAP-particles, the teachings of which are incorporated by reference herein. The compounds and articles of the present invention should be substantially free of those polar diluents or copolymers, and substantially free of those functional groups.

We believe that polar compounds and those other functionalized groups tend to inhibit the desired percolation of the swelling SAP particles from the article. Accordingly,

any substantial quantity of those compounds or groups may negatively impact the SAP-Utilization Rate. Preferably, the compound or article should contain less than 10 weight percent, more preferably less than 5 weight percent, and most preferably less than 1 weight percent, (based upon the dry weight of the compound or article) of any polar compound or any other compound having a functional group that interacts ionically or covalently with the SAP particles.

Another measure of the interaction or adhesion between the SAP particles and the matrix-polymer is whether the addition of the SAP particles to the matrix-polymer increases or decreases its engineering stress response. If the matrix-polymers tend to adhere to the SAP particles, the addition of SAP particles to those matrix-polymers form SAP-containing articles that are more stiff than a similar article made from the unfilled matrix-polymer per se. Such matrix-polymers are defined herein as having a "high Adhesion Factor."

Conversely, matrix-polymers that do not adhere to the SAP particles have the opposite response. The addition of SAP particles to these latter matrix-polymers results in SAP-containing articles that are less stiff than a similar article made from the unfilled matrix-polymer per se. Such matrix-polymers are defined herein as having a "low Adhesion Factor." For the present invention, matrix-polymers with a low Adhesion Factor are preferred.

20 Other Permissible Components

5

15

25

30

The compounds and articles of this invention may contain minor amounts of other components that advantageously affect the properties of those compounds or articles. For example, the compositions and article of this invention may contain various additives, such as nucleating, anti-oxidizing, stabilizing, clarifying, stiffness, blowing, processing, coloring, and/or crystallization-rate agents. These agents are used in a conventional matter and in conventional amounts.

We have found that some surfactants appear to reduce the surface tension and/or contact angle of the other components to enhance the fluid-uptake of the SAP particles without adversely affecting the percolation of the swollen SAP particles from the matrix-polymer. For example, incorporating minor amounts (such as from 0.5 to 5 weight percent, more preferably from 1 to 3 weight percent) of the following surfactants was found to

enhance the absorption of water without adversely affecting the percolation of the swollen SAP particles from the matrix-polymer:

| Surfactant | Chemical Type | Wt. percent | Available from |
|------------------|--|-------------|-------------------------------|
| DOWFAX* 20A42 | Non-ionic, fatty alcohol alkoxylate | 1 to 3 | The Dow Chemical Company |
| DOWFAX 20A64 | Non-ionic, fatty alcohol alkoxylate | 1 to 3 | The Dow Chemical Company |
| Irgasurf™ HL 560 | | 1.5 to 3 | Ciba Specialty Chemicals Inc. |
| DOWFAX 8390 | Mono- and di-alkyl disulfonated diphenyloxide, disodium salt | 1 to 3 | The Dow Chemical Company |
| DOWFAX 20B102 | Non-ionic, fatty alcohol alkoxylate | 1 to 3 | The Dow Chemical Company |
| CARBOWAX* 3350 | Polyethylene glycol | 1 to 3 | The Dow Chemical Company |
| Soap · | Natriumlaurylsufate | 1 to 3 | Fluka-Chemie |
| Tergitol* 15-S-7 | Alkyloxypolyethyleneoxyethanol plus <3 percent of PEG | 1 to 3 | The Dow Chemical Company |
| Triton* DF 12 | Modified polyethoxylated alcohol | 1 to 3 | The Dow Chemical Company |

^{*} Trademark of The Dow Chemical Company

A variety of anti-oxidants known in the art can be used in the normal concentrations. Suitable anti-oxidants include those blends of hindered phenolic antioxidants and organophosphites marketed by Ciba Specialty Chemicals, Inc. under the trade name "Irganox B-225." Suitable amounts of the anti-oxidants are typically less than 1 weight percent, more preferably less than 0.5 weight percent, of the total compound.

Optionally, the compositions or articles of this invention may include various colorants which can be used in the normal concentrations. Suitable colorants include those marketed by Wilson Color S.A. (a business unit of PolyOne Corporation) under the trade name "Wilson 1285-GN-50." Other colorants include zinc oxide or titanium oxide. Suitable amounts of the colorants are typically between 0 and 3 weight percent, more preferably between 0 and 1 weight percent, of the total compound.

15

20

10

5

Description of Interconnected Network and Percolation

Our observation of various articles made in accordance with the present invention have led us to some theories as to how those articles function. It is not our intention to have our invention be limited to any particular theory. Rather, our invention is defined by the scope of our claims below.

Fig. 1 is a diagram showing how film test specimens are prepared for surface and cross-sectional analysis by Scanning Electron Microscopy (SEM), for example, in order to determine the presence of interconnected networks of SAP particles in a matrix-polymer. For a film 10, the test specimen 12 is cut from an interior portion of the film, with the cut-

lines of the test specimen running either in line (cuts 14) with, or perpendicular (cuts 16) to, the machine-direction (18) of the film. The following surfaces of the test specimen (12) are then analyzed by SEM: the cross-section of the film in the machine-direction (20), the cross-section of the film in the transverse-direction (22), and the surface of the film (24). After mounting the specimen on specimen stages, they are sputter coated with about 100 Angstroms of palladium, and then the surface in question is examined with SEM.

Fig. 2 is a SEM micrograph showing an interconnected network of SAP particles in a machine-direction cross-section of a film formed in accordance with this invention.

Numerous SAP particles (40) can be seen dispersed in the matrix-polymer (50). Some of the SAP particles (for example, those labeled 41, 42, 43, 44, and 45) can be seen to be physically contacting one or more of the other SAP particles. Additionally, as a result of the low adhesion between the SAP particles and the matrix-polymer, various spaces or gaps (for example, those labeled 61, 62, and 63) can be seen around some of the SAP particles—providing fluid pathways through the matrix-polymer (50). This combination of particles in physical contact with each other, and the fluid pathways in gaps between SAP particles and the matrix-polymer are representative of a preferred Interconnected Network for the compounds and articles of this invention. Depending upon such factors as the SAP particle size and concentration, the thickness of the compound or article, the Adhesion Factor between the SAP particles and the matrix-polymer, the composition and modulus of the matrix-polymer, and the absence of undesirable components (for example, polar compounds), various Interconnected Networks are possible.

10

15

20

25

30

Figs. 3A, 3B, and 3C are SEM micrographs of the surface of a test specimen cut from a film formed in accordance with this invention after that film had been contacted with deionized water. Fig. 3A shows a large number of crevice-like cavities (70) created across the surface of the test specimen (80) by the percolation of SAP particles out of the matrix-polymer. Some of the cavities (for example, those labeled 71, 72, and 73) appear to be relatively shallow and isolated from the other cavities. Other cavities (for example, those labeled 75, 76, and 77) appear to be deeper. Fig. 3B is a more highly magnified view of one of the deeper cavities (78). The irregular and convoluted shape and the depth of that cavity (78) seem to evidence that the cavity was formed by the successive percolation out of the film of an interconnected network of SAP particles -- resulting in a larger cavity made up of interconnected (or nested) series of smaller cavities. By way of contrast, Fig. 3C is a more

5

10

15

20

25

30

highly magnified view of one of the shallow, more-isolated cavities (74), which appears to have been formed by the percolation of one or a small number of SAP particles that were not in fluid-communication with other SAP particles.

Figs. 4A and 4B are SEM micrographs showing the cross-sections of two test specimens cut from separate portions of the same film formed in accordance with this invention. The film is formed by roll-milling a composition of this invention into a 500 micron film. The composition comprises about 40 parts of SAP particles, Hysorb C3746-1, having a particle size of 20 to 50 microns (determined via microscopy), and about 60 parts of a homogeneous, substantially linear copolymer of ethylene and 1-octene having a density of about 0.857 gm/cm3, a Melt Flow Rate (190° C./2.16 kg) of about 1 gm/10 min., and a 2 percent Secant Modulus of about 7 MPa. The composition also contains 0.2 parts of the antioxidant "Irganox B-225," 1 part of surfactant, DOWFAX 20A64, and 1 part of colorant, Wilson 1285-GN-50.

The film is then divided into two portions -- a control portion and a portion that is submerged within a glass container filled with deionized water. After about 12 hours, the film is removed from the deionized water and dried in a convection oven at 55°C for over 3 hours. Specimens are subsequently sectioned with a razor blade or a glass knife in the machine direction (MD). Fig. 4A shows a MD cross-section of a test specimen cut from the control portion of the film (that is, the portion that was not contacted with water). Similarly, 4B shows a machine-direction cross-section of a test specimen cut from the portion of the film that was contacted with deionized water.

Fig. 4A shows that the machine-direction cross-section of the test specimen (100) cut from the control portion of the film has a large number of SAP particles (110), and various gaps or fluid pathways (120) dispersed throughout the matrix-polymer (130).

Fig. 4B shows the machine-direction cross-section of the test specimen (140) cut from the second portion of the film, after that film had been contacted with deionized water. A few unswollen SAP particles (150) are still evident in the matrix-polymer (160); however, the fact that large numbers of SAP particles have percolated out of the matrix-polymer is evident from both the large number and volume of cavities (170) throughout the cross-section of this test specimen, but also the apparent thinning of the film thickness. The observation of cavities (170) deep into the interior of the specimen (140) is explainable due

to the interconnected network that both provides a pathway for water to penetrate to the SAP particle, and for the swelling SAP particle to percolate out of the matrix-polymer.

A Factor and B Factor

5

10

15

20

25

30

We have discovered that the Max-SAP-Utilization Factor (A Factor) and the SAP-Utilization Rate (B Factor) can be varied by selection of the SAP particle-size and type (for example, the mCC and extractables content of the SAP), the relative concentrations of SAP and matrix-polymer, the type and concentration of appropriate surfactants, and the type and properties (for example, the Adhesion Factor and 2 percent Secant Modulus) of the matrix-polymer.

For most applications, a high A Factor and a high B Factor are desired. The A Factor (when testing the SAP particles and matrix-polymer components of the composition or article in question, in the SAP-Utilization Test with deionized water) is preferably greater than about 60 percent, more preferably above about 70 percent, even more preferably above about 80 percent, and most preferably above about 85 percent. The B Factor (when testing the SAP particles and matrix-polymer components of the composition or article in question, in the SAP-Utilization Test with deionized water) is preferably about 0.02 minutes⁻¹, more preferably above about 0.04 minutes⁻¹, even more preferably above about 0.06 minutes⁻¹, and most preferably above about 0.10 minutes⁻¹. For the same SAP and matrix-polymer components, in an SAP Utilization Test run with 0.9 wt percent saline solution, typically the A Factor will be somewhat (for example, 10 percent) less than in deionized water, however, the B Factor will typically be similar to that in deionized water.

Description of Manufacturing Method

In the present invention, it is desired to disperse the SAP-particles substantially uniformly throughout the matrix-polymer while preferably forming the interconnected network of SAP particles that achieves the desired SAP-Utilization Rate and Max-SAP-Utilization Factor. To incorporate the SAP particles into the matrix-polymer, a variety of melt-processing methods and equipment may be used, such as melt-extrusion with a reciprocating single screw, or batch mixing on Banbury-type or roll-milling equipment (for example, where the compound is used in-line for film or sheet production by calendaring). Compounding via continuous melt mixing processes with subsequent pelletizing are known

and widely used in the plastics industry. However, for the present invention it is important to incorporate the SAP particles into a matrix-polymer under conditions that minimizes or eliminates any contact of the SAP particles with any fluid (for example, water) that would cause the SAP particles to swell. Swelling of the SAP particles not only uses up fluid-absorbing capacity of the article, it also tends to form agglomerates during the compounding or article-formation processing — resulting in poor quality articles. Accordingly, the SAP particles per se should be dry during the compounding, and the compounding and article-formation processing should be conducted under conditions that minimize or eliminate contact between the SAP particles and any fluid that would swell those particles.

5

10

15

.20

25

30

If the SAP particles initially have absorbed moisture, they should be dried before being placed in the feed-hopper. Also, the environment contacting the SAP in the feed-hopper and compounder should be substantially free of any fluid that would swell the SAP particles. Thus, no liquid water or aqueous solution absorbable by the SAP particles should be allowed in contact with the compounds or articles, and any gaseous cooling medium should preferably have less than 30 percent, more preferably less than 20 percent, and most preferably less than 10 percent relative humidity. As the equipment is being heated up or cooled down, it is helpful to isolate the feed-hopper and metering device from any hot air or steam that might be generated in the compounder.

At the same time, however, care must be taken to avoid having the fluid-absorbing articles clump together. Many of the elastic matrix-polymers preferred for use in this invention tend to be sticky or tacky in their molten, semi-molten, or even non-molten state. Therefore, the methods and equipment selected for making the compound and forming the articles should be chosen in view of this tendency.

The present invention also provides a method for forming fluid-absorbing articles that minimizes or eliminates contact between the SAP particles and any fluid that would swell those particles, while at the same time avoids the undesired clumping of the molten, semi-molten, or non-molten masses of SAP-containing composition.

The present invention provides a method for manufacturing a fluid-absorbing article having a fluid-absorbing capacity and a fluid-absorbing rate that are appropriate for the particular end-use application. Usually, it is desired to obtain a homogeneous dispersion and distribution of the fluid-absorbing SAP particles throughout the SAP-containing layer of the article in question. Surprisingly, by careful selection of the components, and the

manufacturing conditions, much higher than expected fluid-absorbing-capacity utilization and fluid-absorbing rates are obtained as compared to the known SAP-containing articles using different components or processing conditions.

5

10

15

20

25

30

To achieve homogeneous dispersion and distribution of the SAP particles into the matrix-polymer, we have found it important to melt-mix these components using compounding equipment that have a high level of distributive mixing. One such apparatus is a reciprocating single-screw compounder, sold by Coperion Buss AG under the trademark "Ko-Kneader." An exemplary, laboratory-scale compounder is model number MDK/E 46-15 L/D, which has a single screw with a diameter of 46 mm and a length of 690 mm (15 times 46 mm). The screw-flights are interrupted 3 times per its 360-degree circumference -in other words, there are three slots cut out of the screw flight, spaced at intervals of 120°, to make the screw look like a series of 3-bladed propellers stacked onto the shaft. These slots in the screw flights allow the mixing pins fixed in the barrel housing to pass through those slots when the screw is rotating and simultaneously also reciprocating (that is, oscillating in axial direction). The shear action (dispersive mixing) takes place primarily in the shear gap between the screw flight and mixing pin. The homogenization (distributive mixing) is achieved through the intense renewal of the melt surface between the screw flights when the mixing pin is separating the melt into two different streams and is combining these with other streams being generated by the next following pin just preceding it.

The components are fed into the compounding mixing chamber through different feed-ports, which are located on the compounder barrel in axial direction. In other words, the individual components are metered via gravimetric metering units (for example, K-Tron LWF units) and are dropping by gravity in tubes, vertically placed over the feed-ports, into the mixing chamber. Preferably, a split-feed arrangement is chosen in order to minimize or prevent formation of SAP agglomerates in the melting zone of the compounder. In particular, the matrix-polymer pellets as well as any antioxidant or other polymer-processing additives are fed into the first feed-port, whereas the SAP powder is fed downstream, into the second feed-port after the matrix-polymer has already molten. In this particular compounding device, approximately 11 L/D of the screw length is still available downstream of the second feed-port to homogeneously incorporate the SAP powder into the matrix-polymer melt.

The requirement to incorporate and to evenly distribute both the SAP and any additives in the matrix-polymer at a temperature below the degradation point of the SAP is achieved by the gentle mixing of the Ko-Kneader compounder. Sufficient mixing is achieved by using a standard screw with 3 restriction rings in the barrel. The screw of the Ko-Kneader has a hollow shaft through which a heating / cooling media can flow to control the temperature of the compound. In addition, this reciprocating single screw compounder with its particular screw design of interrupted screw-flights operates under very low pressure in the mixing chamber and allows the control of the molten compound at a desired low temperature (that is, at or slightly above the melting point of the matrix-polymer).

10

15

20

25

30

After the molten compound has been formed in the compounder, it is fed into a cross-head extruder, which is arranged so the extruder's screw is perpendicular to the screw of the compounder. A suitable extruder for use with the above-described compounder is a cross-head, single screw extruder, named ASV-46, having a diameter of 42 mm and a length of 147 mm (that is, 3.5 L/D times 42 mm). The molten compound is pushed by the reciprocating single screw of the compounder into this extruder. The extruder screw pressurizes the melt and pushes it in continuous flow to a heated extruder head and through the die holes to form molten extrudates. The number and diameter(s) of the die holes are selected, as known in the industry, depending upon the viscosity of the molten compound, the desired shape and size of the molten extrudate, etc.

The method chosen for cooling of the molten extrudate is very important. Firstly, any fluids (for example, water) present that would cause the SAP-particles to swell would pre-maturely use up the absorption capacity of those particles and could disrupt the downstream processing (for example, the extrusion and/or article fabrication processes). Consequently, the most common form of cooling used in the industry (passing the molten extrudates through water) is not satisfactory.

Secondly, many of the types of matrix-polymers preferred for use in the present invention are rather sticky -- not only in the molten or semi-molten state, and as they are being cooled, but also often even after being cooled to a non-molten state at ambient conditions.

In order to avoid having the polymeric extrudates stick to each other (or the equipment), an inorganic powder is applied onto the surface of the molten or semi-molten masses. Preferably, a fine inorganic powder (such as talcum, silicates, silica (SiO2), chalk

(CaCO3), china clay, Kaolin, aluminum tri-hydrate (Al2(OH)3), mica, titanium dioxide, zinc oxide, wollastonite, dolomite, barytes, feldspar, or hydromagnesite) is applied onto at least a portion of the external surface of the molten or semi-molten masses (for example, pellet-shaped or strand-shaped masses exiting a die) prior to or concurrently with the contacting of those masses with a gaseous cooling medium. Preferably, this surface dusting is achieved by blowing around those masses (for example, into the pelletizer hood) high volumes of a cooling gas (for example, compressed, moderate- to low-humidity air) in which the inorganic powder is entrained. For example, the cooling medium can be forced through a bed of the inorganic powder prior to contact of the cooling medium with the molten or semi-molten masses.

5

10

15

20

25

30

The amount of inorganic powder being injected into the pelletizer hood is controlled by the amount of cooling medium flowing into the powder container. The inorganic powder injected into the pelletizer hood adheres to the sticky surface of the formed masses, reducing their tackiness and tendency to form clusters. In a preferred embodiment, additional cooling medium (that is, in addition to that carrying the inorganic powder) is being injected to blow the cooling masses downward resulting in a fast velocity flow that not only cools the masses, but also sweeps out excess inorganic powder that can be separated from the non-molten masses, collected, and then recycled. The cooling masses can be dropped onto conveyors, screens, or belts for sorting, collection, and/or further cooling, while at the same time avoiding contact of the masses with fluids that would cause the SAP particles to swell. The cooled, non-molten masses are then collected in containers for further processing or use. For example, where those masses are pellets, the pellets are stored in bags or other containers (for example, Gaylord boxes, rail-cars, silos, etc.) for storage and shipment and then later fed into article-fabrication equipment (for example, melt-extruders, injection-molding equipment, film-fabricating equipment, etc.) to produce other articles.

In some embodiments of this invention, SAP-containing pellets from compounding process are produced in-line (that is, a pelletizing unit is part of the compounder set-up, either via hot-face-pelletizing or strand-pelletizing). In those embodiments, the molten compound is extruded through a die with multiple holes forming "spaghetti-like" strands, which are then cut into pellet-shaped masses. In a hot-face-pelletizing process, the strands are cut immediately upon exiting the die hole (that is, while still molten) to forming molten pellet-shaped masses (that is, having a round or a lens-type shape). These pellet-shaped

masses are then contacted with the inorganic powder and cooled with the cooling medium. In a strand-pelletizing process, the molten "spaghetti-like" strands exiting the die are contacted with the inorganic powder and cooled with the gaseous cooling medium to form non-molten strands, which are then cut into pellets, usually resulting in cylindrically shaped pellets.

5

10

15

20

25

30

In one preferred embodiment, water-absorbing polymeric extrudates are made by the following procedure: Pellets of the matrix-polymer(s) and an anti-oxidant powder (such as that marketed by Ciba Specialty Chemicals, Inc. under the brand name, Irganox* B-225) are dry blended in a high-speed mixer, and that blend is fed into a first feed-port of a multi-feed-port compounder (such as the reciprocating, multi-flighted screw-type compounder, Model MDK /E 46-15L/D, manufactured by Coperion Buss AG) through a metering unit. As the matrix-polymer is conveyed from the first feed-port to the second feed-port, it is heated so as to form a molten matrix-polymer at the base of the second feed-port. SAP particles are fed into the second feed-port and are blended into the molten matrix-polymer during transport through the compounder to complete the mixing of the matrix-polymer and the SAP particles.

The SAP particles are prepared as follows: Conventional SAP, such as the superabsorbent polymers marketed by BASF AG under the trademark "Hysorb," and more specifically Hysorb grade C-3746-1, or those marketed by The Dow Chemical Company under the trademark "DRYTECH," or more specifically DRYTECH grades S230R fines or S100R fines, are obtained. In general SAP operations, SAP particles that pass through a sieve having openings of about 350 microns are considered "fines." These SAP fines are milled as needed to reduce their particle size and then screened to select only those SAP particles of the desired sizes. If the resulting SAP particles do not have the desired properties (for example, dryness, mCC, or extractables content), they are pre-treated, either before or after the milling and/or screening as described above.

Since the SAP particles tend to absorb humidity from the air, the environment contacting the SAP during preparation of the particles and/or feeding into the compounder should be dry (for example, the air should preferably have less than 30 percent, more preferably less than 20 percent, and most preferably less than 10 percent relative humidity). As the equipment is being heated up or cooled down, it is helpful to isolate the feed-hopper and metering device from any hot air or steam that might be generated in the compounder.

The temperature profile of the compounder is controlled to optimize the compounding and the properties of the molten SAP-containing compound made in the compounder. For example, it is preferred that the temperature of the compounder screw and barrel in the initial zone be kept relatively low — preferable within 10° C. of the melting point of the matrix-polymer, and most preferably 5 to 10° C. below that melting point. The shear energy induced by rotation of the compounding screw raises the temperature of the matrix-polymer to melt it — forming the polymeric melt into which the SAP particles are introduced at the second feed-port. By contrast, at the extrusion head the temperature should be higher to minimize or preclude clogging of the die holes. The temperature at the extruder head is thus between the melting point of the matrix-polymer and the temperature at which the SAP particles would decompose.

Preferably, during start-up of the compounder, the matrix-polymer is introduced first and molten polymer fills the zone(s) of the compounder into which the SAP particles will be introduced. This helps ensure that, in passage through the compounder, the SAP particles are mixed into the matrix-polymer, rather than simply being compacted into agglomerates of SAP-particles that are difficult to disperse in the matrix-polymer.

Once the initial SAP-free quantity of the matrix-polymer has been extruded and removed from the die-face, and the SAP-filled polymer begins exiting the extrusion die, the pelletizer hood is closed to contain the extruded SAP-filled polymer (either in the form of strands or pellets), the inorganic powder, and the cooling medium (that is, dry air).

Description of Various Articles/Forms

10

.15

20

25

30

The composition of this invention can be shaped or fabricated into various forms, including but not limited to films, coatings, sheets, strips, tapes, profiles, ribbons and the like. A film, coating, or sheet of the present invention may be fabricated by any method known in the art, including blown-bubble (for example, simple bubble as well as biaxial orientation techniques such trapped bubble, double bubble, and tenter framing), cast-extrusion, injection-molding, thermoforming, extrusion-coating, profile-extrusion, and sheet-extrusion processes. Simple blown-bubble-film processes are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192. The cast extrusion method is described, for example, in Modern Plastics Mid-October 1989 Encyclopedia

Issue, Volume 66, Number 11, pages 256 to 257. Injection molding, thermoforming, extrusion coating, profile extrusion, and sheet extrusion processes are described, for example, in <u>Plastics Materials and Processes</u>. Seymour S. Schwartz and Sidney H. Goodman, Van Nostrand Reinhold Company, New York, 1982, pp. 527-563, pp. 632-647, and pp. 596-602. The films, sheets, or profiles can be mono-layer or multi-layer structures, with the composition of this invention constituting the innermost layer, the outermost layer, or any intermediate layer in a multi-layer structure.

A strip, tape, and/or ribbon of the present invention can be prepared by any known method, including the direct extrusion processing or by post-extrusion slitting, cutting or stamping techniques. Profile extrusion is an example of a primary extrusion process that is particularly suited to the preparation of tapes, bands, ribbons, pipes, tubes, wires, cables, and the like.

10

15

20

25

30

For the articles of this invention that are in the form of films, sheets, strips, tapes, ribbons, or bands, their thickness (exclusive of any other layer or substrate which does not contain SAP particles) will typically be between 10 and 3000 microns, and more preferably between 15 and 1200 microns. For the films of this invention (which can be monolayer or multi-layer films), the thickness of the SAP-containing layer is most preferably between 20 and 800 microns. We have found that it is desired for those articles that the SAP particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times that thickness, preferably no greater than about 0.6 times that thickness, more preferably no greater than about 0.5 times that thickness, and most preferably no greater than about 0.4 times that thickness. It is contemplated that narrow size ranges of SAP particles (for example, particles that pass through a sieve with openings of 40 microns, but that do not pass through a sieve with openings of 20 microns) may be used in these articles of the present invention. Where narrow particle size ranges are used, SAP particles will typically pass through the largest sieve selected (for example, based upon the desired ratio to the fiber thickness) but not pass through a sieve with openings that are from 0.1 to 0.8 times, preferably from 0.3 to 0.5 times, the size of the openings of the largest sieve. However, it is believed that the presence of very fine SAP particles (that is, much smaller than openings in the sieves that yield the above ratios) with the larger particles (that is, those just passing through the largest sieve openings) may in fact be beneficial. Although not wishing to be limited to any particular theory, we believe that the presence of a broad range of SAP

particle sizes (within the sizes that pass through the specified sieve) may help to establish the desired interconnected network of SAP particles, while maintaining or even enhancing the processability of the composition. For example, the presence of the smaller SAP particles may more readily enable an interconnected network as compared to a similar composition having a narrow, larger range of SAP particle sizes. With a broader range of SAP particle sizes, it appears that a lower concentration of the larger SAP particle sizes may be sufficient (even at an equivalent total SAP concentration) to establish the desired interconnected network. Where a broad range of particle sizes is used, it is preferred that substantially all of the SAP particles used are capable of passing through a sieve having openings of less than the smaller of (a) 150 microns or (b) the above-described size relative to the thickness of the SAP-containing layer or article. For example, for a monolayer film having a thickness of about 200 microns, a preferred SAP particle size range is obtained by milling the "as received" SAP to reduce their overall size, and using only those SAP particles that pass through a sieve having openings between 30 and 120 microns (that is, a ratio between 0.15 and 0.6 times the film thickness). As another example, for a monolayer film having a thickness of about 100 microns, a preferred SAP particle size range is obtained by milling the "as received" SAP to reduce their overall size, and using only those SAP particles that pass through a sieve having openings between 30 and 80 microns (that is, a ratio between 0.3 and 0.8 times the film thickness).

20

25

30

5

10

15

The composition of this invention also can be shaped or fabricated into various fibrous forms, including homofil fibers, bicomponent fibers, nonwovens, yarns, and fabrics. Various homofil fibers can be made from the compositions of the present invention, including staple fibers, spunbond fibers or melt-blown fibers (using, for example, systems as disclosed in USP 4,340,563, 4,663,220, 4,668,566 or 4,322,027, and gel-spun fibers (for example, the system disclosed in USP 4,413,110). Staple fibers can be melt spun into the final fiber diameter directly without additional drawing, or they can be melt spun into a larger diameter and subsequently hot or cold drawn to the desired diameter using conventional fiber-drawing techniques.

Bicomponent fibers can also be made from the compositions of this invention. Such bicomponent fibers have the composition of the present invention in at least one portion of the fiber. For example, in a sheath/core bicomponent fiber (that is, one in

which the sheath concentrically surrounds the core), the composition of this invention can be in either the sheath or the core. Preferably, the compositions of this invention are used in a component that is exposed to the surrounding environment (for example, the internal layer in a hollow fiber, or the sheath in a sheath-core bicomponent fiber). Other types of bicomponent fibers are within the scope of the invention as well, and include such structures as side-by-side conjugated fibers (for example, fibers having separate regions of polymers, wherein the compositions of the present invention comprises at least a portion of the fiber's surface).

5

10

15

20

25

30

The shape of the fiber is not limited. For example, typical fiber has a circular cross-sectional shape, but sometimes fibers have different shapes, such as a trilobal shape, or a flat (that is, "ribbon" like) shape. The fiber embodiments of this invention are not limited by the shape of the fiber.

Fiber diameter can be measured and reported in a variety of fashions. Generally, fiber diameter is measured in denier per filament. Denier is a textile term which is defined as the grams of the fiber per 9000 meters of that fiber's length. Monofilament generally refers to an extruded strand having a denier per filament greater than 15, usually greater than 30. Fine-denier fiber generally refers to fiber having a denier of about 15 or less. Microdenier (aka microfiber) generally refers to fiber having a diameter not greater than about 100 micrometers. For the fibers of this invention, the diameter can be widely varied. The fiber denier, however, can be adjusted to suit the capabilities of the finished article and as such, would preferably be: from 0.5 to 30 denier/filament for melt blown; from 1 to 30 denier/filament for spunbond; and from 1 to 20,000 denier/filament for continuous wound filament.

We have found that it is desired for those fibrous articles that the SAP particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the diameter of the spinneret (100 to 1,000 micron) used to form the fiber that contains the composition of this invention, preferably no greater than about 0.7 times that diameter, more preferably no greater than about 0.6 times that diameter, and most preferably no greater than about 0.5 times that diameter.

As stated above for film articles, it is contemplated that narrow size ranges of SAP particles may be used in the fibrous articles of the present invention, and also that the presence of very fine SAP particles (that is, much smaller than openings in the sieves that

yield the above ratios) with the larger particles (that is, those just passing through the largest sieve openings) may in fact be beneficial. Where narrow particle size ranges are used, SAP particles will typically pass through the largest sieve selected (for example, based upon the desired ratio to the fiber thickness) but not pass through a sieve with openings that are from 0.05 to 0.5 times, preferably from 0.1 to 0.3 times, the size of the openings of the largest sieve.

Fabrics made from the fibers of this invention include woven, nonwoven and knit fabrics. The fibers of this invention can be used with other fibers such as PET, nylon, cotton, Kevlar™ fibers, etc. to make fabrics. Nonwoven fabrics can be made by various methods, for example spunlaced (or hydrodynamically entangled) fabrics as disclosed in USP 3,485,706 and 4,939,016, carding and thermally bonding staple fibers; spunbonding continuous fibers in one continuous operation; or by melt blowing fibers into fabric and subsequently calandering or thermally bonding the resultant web. These various nonwoven fabric manufacturing techniques are well known to those skilled in the art and the present invention is not limited to any particular method. Other structures made from such fibers are also included within the scope of the invention, including for example blends with other fibers (for example, poly(ethylene terephthalate) or cotton).

10

15

20

25

30

Fabricated articles which can be made using the articles of this invention include composite articles (for example, diapers) that have fluid-absorbing portions. Attachment of the various articles of this invention to substrates (including fibers, fabrics, foams, nonwovens, films, sheets, or other structures) can be done by various means, including but not limited to melt-bonding or with adhesives.

To make a foam article of this invention, a blowing agent is incorporated into the composition (either concurrently with or before or after incorporation of the SAP particles into the matrix-polymer) by any means known in the art (such as with an extruder, mixer, or blender during the compounding of the composition). The blowing agent is added under pressurized (that is, super-atmospheric) conditions sufficient to prevent premature substantial expansion of the melt polymeric material and to generally disperse the blowing agent homogeneously within the composition. Optionally, a nucleating agent may be blended in the polymer melt or dry blended with the polymer material prior to melting. The composition is then allowed to expand to form the desired foam article (for example, a foamed sheet, profile, bun, or other form), by methods well known in the art.

Any conventional blowing agent may be used to prepare the foam articles of this invention. USP 5,348,795 discloses a number of suitable blowing agents at column 3, lines 15-61, the teachings of which are incorporated herein by reference. USP 5,527,573 also discloses a number of suitable blowing agents at column 4, line 66 through column 5, line 20, the teachings of which are incorporated herein by reference. Preferred blowing agents include aliphatic hydrocarbons having 1-9 carbon atoms, especially propane, n-butane and isobutane, more preferably isobutane. Suitable blowing agents including the one marketed by Lehmann & Voss & Co. under the tradename "Luvopur 40.G-UT."

10 End-Use Applications

5

15

20

25

30

Hygiene and medical applications in which the fluid-absorbing articles of this invention would function as a liquid absorber include feminine sanitary articles, wound care, medical gowns, diaper core, wound dressings, and bandages. In addition, the combination of elasticity and high WVTR obtainable with the fluid-absorbing articles of this invention may be useful in disposable infant diapers and adult incontinence undergarments, for example, because its elasticity would provide for a form-fitting comfort. With conventional technology, breathability and elasticity tend to be mutually exclusive.

In food-packaging applications, the fluid-absorbing articles of this invention could function as part of a liquid-absorbing device, such as a meat soaker laminate/film or as an injection-molded tray.

In house-wrap or other construction end-use applications, the fluid-absorbing articles of this invention could function as a humidity buffer. For example, the articles could slowly absorb and release moisture with climate changes and thus moderate humidity conditions in the adjacent environment (for example, the interior of the house).

Conventional house wraps only allow for water vapor transport and have no water-retention capacity.

In agricultural end-use applications, the fluid absorbing articles of this invention could function as a pesticide or fungicide carriers, which are released from for example mulch films in a controlled manner, as the humidity increases below such films laid over the agricultural fields and will cause the SAP particles to swell and consequently percolate out of the articles.

Elastic, Porous Films or Membranes

5

15

20

25

30

The above-described SAP-containing articles of this invention can also be used as an intermediate in the formation of porous articles, because (as shown in Figs. 3A, 3B, 4B, and 5A) upon contact with a suitable fluid a large percentage of the SAP particles will swell and percolate out of the articles, leaving a network of pores in the article where the SAP particles had been. Porous articles are used in a variety of end-use applications, including but not limited to hygiene or medical applications, filtration of fluid/solid systems, fluid separations, water separation or purification, packaging, environmental processes, smart membranes, and the like. By appropriate selection of the SAP particle size, particle-size distribution, and concentration, porous articles with a wide variety of macro-porous and/or micro-porous configurations are possible. For example, the porous articles of this invention may have water-vapor-transmission rates (WVTR) that are from 10 to 1,000 times the WVTR of the same article made with all the same components, except no SAP particles.

In a preferred embodiment of this invention, elastic, porous films or membranes are made from the above-described films or sheets of this invention that has been made with an elastic matrix-polymer (in particular those elastic ethylene-based or propylene-based polymers described above), by contacting those films or sheets with water so as to cause at least a portion of the SAP particles to percolate out of the film or sheet, thereby leaving a plurality of pores in the film or sheet. The resulting porous film or sheet can be used directly or further prepared (for example, by stretching, ion-exchange, crosslinking, impregnation with various catalytic or ionic agents, or the like) for use as a porous film or membrane.

EXAMPLES

The following examples are given to illustrate various embodiments of the invention. They do not intend to limit the invention as otherwise described and claimed herein. All numerical values are approximate. When a numerical range is given, it should be understood that embodiments outside the range are still within the scope of the invention unless otherwise indicated. Most of the methods or tests were performed in accordance with an ASTM standard, if applicable, or known procedures. All parts and percentages are by weight unless otherwise indicated.

Examples 1 to 10

10

A series of films are produced in two steps: (1) melting of the matrix-polymer(s) and incorporation of the SAP particles and other components of the formulation into the molten matrix-polymer to form a molten compound, and (2) homogenization and film production with this molten compound on a 2-roll mill. The first step is done in an Banbury-type internal mixer (made by Werner+Pfleiderer GmbH) which has a 2-liter capacity and is equipped with a double jacket through which hot oil is circulating for temperature control. The first step is accomplished as follows:

- (a) weigh all components of the formulation at the right ratio for a total amount of 600 grams and keep each component in a separate container;
 - (b) add the matrix-polymer components (that is, the base matrix-polymer and masterbatches containing the colorant) plus antioxidant(s) into the preheated internal mixer;
- (c) close the mixer and run it for about 10 minutes to melt the matrix-polymer
 component(s), and to incorporate and homogeneously distribute the antioxidant and colorant throughout the molten compound; and
 - (d) stop and open the mixer, and add all other components (that is add the SAP particles, surfactants, etc.) by simply pouring these components onto the top of the molten compound; and
- 20 (e) close the mixer and run it for another 10 minutes to finish incorporating the components into the compound.

The second step is done on a Dr. Collin roll mill (type W 150 M), equipped with two bowls that are preheated to an appropriate temperature. The second step is accomplished as follows:

- 25 (f) transfer the molten finished compound from the mixer in step (e) into the space between and on top of the bowls of the roll-mill;
 - (g) extrude the molten finished compound through the roll-mill to form a molten or semi-molten sheet of about 5 millimeters, then remove that sheet from the roll mill and cut approximately 100 grams from it;
- 30 (h) return that 100 gram piece of molten or semi-molten sheet into the space between and on top of the bowls of the roll-mill

(i) run the roll-mill using a gap of about 0.5 millimeters (500 microns) to further mix the molten compound until a homogenous melt layer is visible on the front bowl of the roll mill,

(j) close the gap between the roll-mill bowls to gap necessary to produce the desire film thickness. For example, in order to obtain a non-molten film of about 0.2 millimeters [200 microns] when the matrix-polymer is elastic, the gap is set at about 0.15 mm. Due to the elasticity of the molten matrix-polymer, it expands (that is, swells) after exiting the gap between the bowls of the roll-mill;

5

20

25

30

- (k) the molten film on the front bowl is cut with a spatula across its width (axial direction) and removed by pulling the film away from the bowl (that is, peeling it off from the bowl) in a horizontal direction and at approximately the same speed as the bowl rotational speed to minimize draw down;
 - (1) the film cooling starts immediately in dry air at ambient conditions (relative humidity about 50 percent and temperature about 20° C.);
- 15 (m) the film is laid onto a flat surface (for example a table or copper plate for good heat transfer and quick cooling) to allow the film to solidify as it cools to ambient temperatures.

Steps (g) through (m) are repeated until enough film samples are made.

Each of the compounds used in forming the approximately 200 micron-thick films contains 60 parts by weight of the particular matrix polymer, 0.2 parts by weight of the anti-oxidant, Irganox B-225, 1 part by weight of the DOWFAX 20A64 surfactant, 1 part by weight of the colorant, Wilson 1285-GN-50, and 40 parts of SAP particles. The SAP particles are prepared by taking the SAP marketed by BASF AG under the tradename "Hysorb C 3746-1," having a particle size of 20 – 50 microns (determined via microscopy). Each of the compounds made for Examples 1 through 10 has a low Adhesion Factor.

Test specimens (cut from each of these films as described with respect to Figs. 1A and 1B) are then tested using the SAP-Utilization Test with deionized water. Table 1 summarizes the averages of the SAP-utilization data (calculated by equation I) from the triplicate test specimens at time intervals of 1, 10, and 180 minutes. The A Factor and B Factor are calculated as described above by fitting all the SAP-utilization data (that is, at intervals of 1, 3, 10, 30, 100, and 180 minutes) to the equation (II).

| Ex. | TABLE 1 Ethylene-based Copolymers | MFR ASTM D1238 190° C./2.16 kg. | Density (g/cm³) | SAP parts | 2% Secant Modulus (MPa) | 1 min. (%) | 10 min. (%) | 180 min. (%) | A Factor | B Factor (1/min) |
|-----|--|---------------------------------------|--------------------|--------------|-------------------------------|------------------|-------------------|--------------------|----------|------------------------|
| 1 | Engage* POE 8842 | ı | 0.857 | 40 | 7 | 40 | 56 | 91 | 90±5 | 0.04 |
| 2 | AFFINITY** EG 8100 | 1 | 0.870 | 40 | 10 | 33 | 57 | 78 | 76±5 | 0.06 |
| 3 | AFFINITY VP8770 | 1 | 0.885 | 40 | 25 | 28 | 52 | 79 | 78±5 | 0.04 |
| 4 | AFFINITY PL 1880 | 1 | 0.902 | 40 | 92 | 25 | 54 | 87 . | 83±5 | 0.04 |
| 5 | AFFINITY FM 1570 | 1 | 0.915 | 40 | 163 | 25 | 55 | 84 | 84±5 | 0.03 |
| 6 | ethylene-styrene copolymer**** | 1 . | 0.939 | 40 | 9 | 22 | 44 | 78 · | 74±5 | 0.03 |
| Ex. | | 230° C./2.16 kg. | | | | | | | | |
| 7 | 86/14 wt% | 2 | 0.857 | 40 | 23 | 8 | 18 | 76 | 75±5 | 0.03 |
| 8 | propylene/ethylene 89/11 wt% | 2 | 0.865 | 40 | 52 | 10 | 35 | 79 | 74±5 | 0.05 |
| . 9 | propylene/ethylene 95/5 wt% propylene/ethylene | ž . | 0.877 | 40 | 262 | 26 | 53 | 76 | 77±5 | 0.02 |
| 10 | 98/2 wt% propylene/ethylene | 6 | 0.897 | 40 | 588 | 30 | 43 | 78 | 76±5 | 0.01 |

- * "Engage" is a trademark of DuPont Dow Elastomers L.L.C. This Engage polymer is an elastic, homogenous, substantially linear copolymer of ethylene and octene made in accordance with the teachings of US Patents 5,272,236; 5,278,272; and 5,665,800.
- ** "AFFINITY" is a trademark of The Dow Chemical Company. These AFFINITY polymers are different grades of elastic, homogenous, substantially linear copolymers of ethylene and octene made in accordance with the teachings of US Patents 5,272,236; 5,278,272; and 5,665,800.
- *** These propylene-based copolymers are different grades of isotactic polypropylene homopolymers made in accordance with the teachings of US patent application Serial Number 10/139,786, filed on May 5, 2002. Each grade has a different (above-indicated) ratio of propylene to ethylene monomer units, but each grade is characterized as having: 13C NMR peaks at 14.6 and 15.7 ppm, the peaks of about equal intensity; and a B-value in excess of about 1.3.
- **** The ethylene-styrene interpolymer is an elastic, substantially random copolymer of ethylene and styrene made in accordance with the teachings of US Patent 6,190,768, having a MFR (ASTM D-1238, 190° C/2.16 kg.) of 0.7 gm/10 min. and 41.1 weight percent styrene units.

Examples 11 to 14

5

10

15

20

Another series of films are produced as described above for Examples 1 to 10.

As indicated in Table 2, the compositions of the compounds used in forming those films have the indicated parts (by weight) of matrix-polymer, specifically AFFINITY EG 8200 ethylene copolymer having a density of 0.870 gm/cm3, and a MFR of 5 gm/10 min (ASTM D1238, 230° C./2.16 kg.); 0.2 parts by weight of the anti-oxidant, Irganox B-225, 1 part by weight of colorant Wilson 1285-GN-50, and the specified parts of DOWFAX

20A64 surfactant. Each of the compounds made for Examples 11 through 14 has a low Adhesion Factor.

Test specimens (cut from each of the films as described with respect to Figs. 1A and 1B) is then tested using the SAP-Utilization Test with saline (0.9 wt.% NaCl). Table 2 summarizes the averages of the SAP-utilization data (calculated by equation I) from the triplicate test specimens at time intervals of 1, 10, and 180 minutes. The A Factor and B Factor are calculated as described above by fitting all the SAP-utilization data (i.e., at intervals of 1, 3, 10, 30, 100, and 180 minutes) to the equation (II).

| | TABLE 2 | | | | 2% Secant | 1 | 10 | 180 | Α | В |
|-----|-----------------------|--------------------|------------------|--------------|------------------|-------------|-------------|-------------|---------------|-------------------|
| Ex. | Matrix-Polymer* Parts | Surfactant Type | Surfactant parts | SAP parts | Modulus (MPa) | min. (%) | min. (%) | min. (%) | Factor (%) | Factor (1/min) |
| 10 | 50 | none | 0 | 50 | 10 | 41 | 77 | 92 | 89±5 | 0.13 |
| 12 | 50 | 20A42 | 2 | 50 | 10 | 34 | 83 | 89 | 82±7 | 0.15 |
| 13 | 40 | 20A42 | . 2 | 60 | 10 | 26 | 81 | 87 | 86±5 | 0.17 |
| 14 | 50 | 20442 | 3 | 50 | 10 | 34 | 77 | 91 | 84±5 | 0.11 |

* This matrix-polymer is an elastic, homogenous, substantially linear copolymer of ethylene and octene made in accordance with the teachings of US Patents 5,272,236; 5,278,272; and 5,665,800, having a density of 0.870 gm/cm³ and a MFR of 5 gm/10 min (ASTM D1238, 230° C/2.16 kg.) that is available from The Dow Chemical Company under the tradename "AFFINITY EG 8200."

15 Example 15 and Comparative Example A

5

20

25

For Example 15, another approximately 200 micron-thick film is produced by the method described above for the films of Examples 1 through 10. The compound used to form the film contains 60 parts by weight of the particular matrix-polymer, 0.2 parts by weight of the anti-oxidant, Irganox B-225, 1 part by weight of DOWFAX 20A64 surfactant, 1 part by weight of the colorant, Wilson 1285-GN-50, and 40 parts of SAP particles. The SAP particles are prepared by taking the SAP product, called "DRYTECH S230R fines" and milling those fines one or more times to reduce the particle size, and then screening out any particles that will not pass through a sieve with openings of about 150 microns, and screening out any particles that will pass through a sieve with openings of about 75 microns. Thus, the SAP particle size range is between 75 and 150 microns. The compound is determined to have a low Adhesion Factor.

For Comparative Example A, an approximately 700 micron-thick cast film is made from a compound in accordance with the teachings of US patent application publication

2002/0039869 A1 (Achille) -- specifically example 15 of that publication. The compound contains 60 parts by weight of the matrix-polymer, and 40 parts by weight of SAP particles. The SAP particles are "as received" SAP marketed by Stockhausen under the tradename "CABLOC 80HS" having a particle size distribution between 1 and 100 microns. The matrix-polymer is a 50:50 blend of two ethylene-acrylic acid products (specifically grades 3460 and 5980) marketed by The Dow Chemical Company under the trademark "PRIMACOR." The compound has a high Adhesion Factor.

5

10

15

20

25

30

Portions of those films are tested using the SAP-Utilization Test, to determine their respective A Factor and B Factor. Example 15 has a high A Factor (100 percent) as compared to Comparative Example A (29 percent), in part due to the difference in film thickness, but also due to matrix-polymer adhesion to the SAP particles. Their B Factors are 0.23 and 0.02 minutes⁻¹, respectively.

Samples of those films are then submerged within a glass container filled with deionized water. After about 12 hours, the films are removed from the deionized water and dried in a convection oven at 55°C for over 3 hours. The samples are mounted on specimen stages, sputter coated with about 100 Angstroms of palladium, and then their top surfaces are examined with SEM.

Figs. 5A and 5B are SEM micrographs showing the top surface (200) of the film of Example 15 and the top surface (300) of the film of Comparative Example A after contacting those surfaces with water as described above. Fig. 5A shows the numerous crevice-like cavities (202) that form in the film of Example 15 of this invention, as contact with the water causes the SAP particles to swell and percolate out of the matrix-polymer, leaving a porous film. Fig. 5B shows some crevice-like cavities (302) in the film of Comparative Example A, but these are far fewer in number and size than the cavities (202) evident in Fig. 5A.

Examples 16, 17, and Comparative Examples B and C

For Examples 16 and 17, another approximately 200 micron-thick film is produced by the method described above for the films of Examples 1 through 10. The compound used in forming that film contains 60 parts by weight of the same matrix polymer as used in Example 1, 0.2 parts by weight of the anti-oxidant, Irganox B-225, 1 part by weight of soap (natriumlaury)sulfate), and 40 parts by weight of SAP particles. The SAP particles are those

5

10

20

25

30

marketed by BASF under the tradename "Hysorb C-3746-1," having a particle size between 20 and 50 microns (measured by microscopy).

For Example 16, a portion of that film is submitted for determination of its watervapor-transmission rate (WVTR) using an automated water vapor transmission rate test equipment, specifically the model "Lyssy L80-4000J" available from LYSSY AG. The film sample is placed on a Lyssy cardboard mask with 10 holes of 25 mm² open surface, through which the water vapor can transmit. The cardboard mask with the film is clamped between two chambers: one chamber contains a dry atmosphere; the other an atmosphere of high humidity. To prevent any significant leakage, a clamping pressure of approximately 70 kPa is applied on the face of rubber gaskets, the mask with the film sample clamped in-between. In the "humidity chamber," an essentially saturated atmosphere is achieved by using liquid water within the chamber filled to a level that the distance between the liquid and the specimen is small (ca. 1 - 3 mm), yet with no direct contact between liquid and specimen. The "dry chamber" is connected to a source of purge gas (clean air), which flows through this chamber until it is dried to a relative humidity of 5 percent or less. Then the dry cell is isolated by valves and the rate of change of its humidity is measured and plotted, that is the accumulation of moisture over time is plotted. This change in relative humidity in this chamber is measured by a humidity sensor and indicator, based on an electrical resistance element. The rate of change of the moisture in the dry cell is determined by the time taken for the concentration to change between two selected levels. The apparatus is first calibrated by using a film of known permeability of which the permeation curves is plotted. The actual water vapor transmission rate is obtained by converting the readings of the values obtained with the help of the calibration curve.

For Example 17, a portion of that same film is first contacted with deionized water by submerging the film for a period of about two hours to cause a majority of the SAP particles to swell and percolate out of the film. After gently removing the percolated SAP-gel from the film surface, and drying the film, the film is submitted for determination of its WVTR.

For Comparative Examples B and C, two other, approximately 200 micron-thick, films are produced by the method described in Examples 1 through 10 for comparison with Examples 16 and 17. The compounds used to produce those films have no SAP particles; however, they are made with 100 parts of a very similar matrix-polymer (an elastic,

homogenous, substantially linear copolymer of ethylene and octene made in accordance with the teachings of US Patents 5,272,236; 5,278,272; and 5,665,800 that has a density of 0.863 gm/cm3, and a MFR of 2.5 (ASTM D-1238, 190° C./2.16 kg.), and they each have about 0.2 parts of an antioxidant. The compound of Comparative Example B also contains 0.9 parts of glass beads (Expancel) and the compound of Comparative Example C also contains 0.8 parts of silicon dioxide (Sipernat 320). These films are submitted for determination of their WVTR.

The WVTR data is summarized in Table 3.

15

20

25

| • | TABLE 3 | | MFR | | • | |
|------------|---------------------|----------------------------------|-------------------------------|--------------------|--------------|-------------------|
| Ex. | Description | Ethylene-based Matrix-polymer | ASTM D1238 190° C/2.16 kg. | Density (g/cm³) | SAP parts | WVTR gm/m²/day |
| 16 | Pre-water contact | Engage* POE 8842 | 1 | 0.857 | 40 | 60 <u>+</u> 10 |
| 17 | After water contact | Engage* POE 8842 | . 1 | 0.857 | ** | 168 <u>+</u> 15 |
| B · | No SAP particles | Ethylene octene*** | · 2.5 | 0.863 | 0 | 17 <u>+</u> 2 |
| С | No SAP particles | Ethylene octene*** | 2.5 | 0.863 | 0 . | 8 <u>+</u> 2 |

- * "Engage" is a trademark of DuPont Dow Elastomers L.L.C. This Engage polymer is an elastic,

 homogenous, substantially linear copolymer of ethylene and octene made in accordance with the teachings

 of US Patents 5,272,236; 5,278,272; and 5,665,800.
 - ** The SAP concentration before washing is 40 parts; however, after contacting with deionized water, most of the SAP particles have swollen and percolated out of the film.
 - *** This ethylene-octene copolymers is an elastic, homogenous, substantially linear copolymer of ethylene and octene made in accordance with the teachings of US Patents 5,272,236; 5,278,272; and 5,665,800.

Example 16 demonstrates that the WVTR of an SAP-containing film of this invention is significantly higher than the WVTR of comparable films (Comparative Examples B and C) without the SAP-particles. Example 17 demonstrates that, after contacting SAP-containing film of this invention with water to swell and percolate the SAP-particles out, the resulting porous film has a WVTR that is even higher than the original SAP-containing film. The films of Examples 16 and 17 retain their elasticity and other attributes of useful films.

Although the invention has been described in considerable detail, this detail is for the purpose of illustration. Many variations and modifications can be made on the invention as described above without departing from the spirit and scope of the invention as

described in the appended claims. The teachings of the U.S. patents and U.S. patent applications identified above are incorporated herein by reference.

WHAT IS CLAIMED IS:

5

10

15

20

25

30

1. A method for manufacturing a fluid-swellable non-molten mass, comprising the steps of:

- (a) providing a plurality of fluid-swellable absorbent particles;
- (b) incorporating those absorbent particles into at least one molten matrix-polymer to form a molten compound, which matrix-polymer (as measured in accordance with ASTM D638-01) has a 2 percent secant modulus of about 60 MPa or less;
- (c) processing that molten compound to form at least one molten or semi-molten mass having an external surface;
- (d) applying an inorganic powder onto at least a portion of the external surface of the molten or semi-molten mass; and
- (e) cooling the molten or semi-molten mass with a cooling medium that is substantially free of any fluid that would swell the absorbent particles, so as to form a non-molten mass.
- 2. The method of claim 1 wherein the at-least-one-molten or semi-molten mass formed in step (c) is a plurality of molten or semi-molten pellet-shaped masses to the external surface of which the inorganic powder is applied in step(d).
- 3. The method of claim 1 wherein the at-least-one-molten or semi-molten mass formed in step (c) is a plurality of molten strand-shaped masses, at least a portion of the external surface of those molten masses is contacted with the inorganic powder in step (d) and cooled to form a plurality of non-molten strands in step (e), and wherein the method further comprises cutting those non-molten strands to form a plurality of non-molten pellets.
- 4. The method of claim 1 wherein the at-least-one-molten or semi-molten mass formed in step (c) is in the form of at least one of the shapes selected from the group consisting of fibers, films, molded articles, foams, sheets, profiles, nonwovens, or any laminate or composite containing one or more of those shapes.
- 5. The method of claim 1 wherein the inorganic powder is selected from the group consisting of calcium carbonate (CaCO3), silicates, silica (SiO2), talcum, china clay, Kaolin, aluminum tri-hydrate (Al2(OH)3), mica, titanium dioxide, zinc oxide, wollastonite, dolomite, barytes, feldspar, or hydromagnesite).

6. The method of claim 1 wherein the inorganic powder is applied to the molten or semi-molten mass prior to or concurrently with the cooling of that molten or semi-molten mass by the cooling medium.

7. The method of claim 4 wherein (1) the shape of the non-molten mass comprises a film, sheet, molded article, or profile having a thickness, and (2) the absorbent particles provided in step (a) are of a size that will all pass through a sieve with openings that are about 0.8 or less times the thickness of that shape.

5

10

15

20

25

- 8. The method of claim 1 wherein the matrix-polymer has a 2 percent Secant Modulus of about 50 MPa or less.
- 9. The method of claim 1 wherein absorbent particles provided in step (a) are first treated, prior to their incorporation into the matrix-polymer, in order to control the content of extractable-polymers to less than about 20 weight percent (based upon the dry weight of the absorbent particles), and wherein that treating is selected from the group consisting of heat-treating, surface crosslinking, ionic crosslinking, or a combination of those treatments.
- 10. The method of claim 1 wherein the absorbent particles provided in step (a) are first treated, prior to their incorporation into the matrix-polymer, in order to control their modified centrifuge capacity (mCC) to between 20 and 50 grams per gram, and wherein that treating is selected from the group consisting of heat-treating, surface crosslinking, ionic crosslinking, or a combination of those treatments.
- 11. The method of claim 1 wherein the size of the absorbent particles provided in step (a) are sufficiently small to pass through a 150-micron sieve.
- 12. The method of claim 1 wherein (1) the plurality of absorbent particles provided in step (a) are sufficient to comprise between 20 and 70 weight percent of the molten compound, and (2) the molten compound consists essentially of the absorbent particles, 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, 0 to 5 weight percent of one or more anti-oxidants, and the at least one matrix-polymer.
- 13. The method of claim 1 wherein the absorbent particles are at least partially embedded within the matrix-polymer such that when the non-molten mass is later contacted with a fluid capable of swelling the absorbent particles, at least a portion of those absorbent particles will release from the matrix-polymer as those absorbent particles swell.

14. The method of claim 1 wherein the absorbent particles are at least partially embedded within the matrix-polymer to form an interconnected network of those particles within the matrix-polymer such that when the non-molten mass is later contacted with a fluid capable of swelling the absorbent particles, at least a portion of those absorbent particles will release from the matrix-polymer as those absorbent particles swell and that release will expose other absorbent particles that are interconnected with the released particles.

- 15. The method of claim 1 in which the components of the molten compound, when tested in the SAP-Utilization Test with deionized water, have a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.
- 16. The method of claim 1 in which the molten compound is substantially free of polar compounds or any polymer having a polar-functional group or other functional group that interacts ionically or covalently with the absorbent particles.
- 17. The method of claim 1 in which the absorbent particles and the matrix-polymer, when tested in the Adhesion Test, have a low Adhesion Factor.
- 18. An article comprising at least one non-molten mass obtainable by the method of any of claims 1 through 17.
 - 19. The article comprising the non-molten mass of claim 18 attached to a substrate.
 - 20. A composition of matter comprising:

5

10

. 15

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those absorbent particles being sufficiently small to pass through a 150-micron sieve; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which those absorbent particles are at least partially embedded so as to initially constrain those absorbent particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those absorbent particles from the matrix-polymer when those absorbent particles are swollen by contact with fluid, which composition (when tested in the SAP-Utilization Test with deionized water) has a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.
 - 21. A fabricated article made from the composition of Claim 20.

- 22. The fabricated article of Claim 21 in the form of a film.
- 23. The fabricated article of Claim 21 in the form of a fiber.
- 24. The fabricated article of Claim 21 in the form of a molded article.
- 25. The fabricated article of Claim 22 in the form of a foam.
- 5 26. The composition of Claim 21, further comprising from 0.5 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and from 0 to 5 weight percent of one or more anti-oxidants.
- 27. The composition of Claim 26 wherein that composition consists essentially of those absorbent particles, those matrix-polymers, those surfactants, and those anti-oxidants.
 - 28. A composition of matter comprising:

15

20

25

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those particles being sufficiently small to pass through a screen with openings of 150 microns; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which the absorbent particles are at least partially embedded to form an interconnected network of those particles within the matrix-polymer so as to initially constrain the particles but, upon contact with a fluid that swells those particles, permit the release of fluid-swollen absorbent particles from the matrix-polymer and exposure of other absorbent particles that are interconnected with the released particles,

wherein the composition is substantially free of polar compounds or any polymer having a polar-functional group or other functional group that interacts ionically or covalently with the absorbent particles.

- 29. A fabricated article made from the composition of Claim 28.
- 30. The fabricated article of Claim 29 in the form of a film.
- 31. The fabricated article of Claim 29 in the form of a fiber.
- 32. The fabricated article of Claim 29 in the form of a molded article.
- 30 33. The fabricated article of Claim 29 in the form of a foam.

34. The composition of Claim 28, further comprising from 0.5 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and from 0 to 5 weight percent of one or more anti-oxidants.

- 35. The composition of Claim 34 wherein that composition consists essentially of those absorbent particles, those matrix-polymers, those surfactants, and those anti-oxidants.
 - 36. An article having a thickness, comprising:

5

- 10

15

20

25

30

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those particles being sufficiently small to pass through a screen with openings of 150 microns; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which the absorbent particles are at least partially embedded to form an interconnected network of those particles within the matrix-polymer so as to initially constrain the particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those fluid-swollen absorbent particles from the matrix-polymer and exposure of other absorbent particles that are interconnected with the released particles, and
- (c) 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and

wherein the article is substantially free of polar compounds or any polymer having a polarfunctional group or other functional group that interacts ionically or covalently with the absorbent particles.

- 37. The article of claim 36 in which those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that article.
- 38. The article of claim 36 in which those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram.
- 39. The article of claim 36 in which those absorbent particles have a content of extractable polymers no greater than about 20 weight percent (based upon the dry weight of the absorbent particles).

40. The article of claim 36 in which that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less.

41. The article of claim 36 in which that at least one matrix-polymer is one or more elastic polymers selected from the group consisting of an ethylene-based polymer or interpolymer, a propylene-based polymer or interpolymer, ethylene-propylene-diene monomer (EPDM) polymers, styrene block copolymers, hydrogenated styrene block copolymers, and blends of any one or more of the foregoing polymers or interpolymers.

5

10

15

20

25

- 42. The article of claim 36 in which that at least one matrix-polymer comprises one or more ethylene-based interpolymers formed by inter-polymerization of ethylene with one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule.
- 43. The article of claim 42 in which the at least one matrix-polymer comprises at least one homogeneous, substantially linear interpolymer of ethylene with at least one alphaolefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³, and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.
- 44. The article of claim 42 in which the at least one matrix-polymer comprises at least one homogeneous, linear interpolymer of ethylene with at least one alpha-olefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³ and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.
- 45. The article of claim 36 in which that at least one matrix-polymer comprises one or more propylene-based interpolymers formed by inter-polymerization of propylene with one or more comonomers selected from the group consisting of ethylene and alpha-olefin comonomers having between 4 and 20 carbon atoms per molecule.
- 46. The article of claim 45 in which that at least one matrix-polymer comprises at least one elastic, isotactic polypropylene homopolymer or interpolymer characterized as having: a MFR (ASTM D-1238, 230° C./2.16 kg.) less than about 100 gm/10 minutes; 13C NMR peaks at 14.6 and 15.7 ppm, the peaks of about equal intensity; and a B-value in excess of about 1.3, and wherein the interpolymer has between 8 and 20 weight percent ethylene-monomer units.
- 47. The article of claim 36 in which that at least one matrix-polymer comprises at least one interpolymer formed by inter-polymerization of ethylene, a vinylidene aromatic

comonomer, and optionally one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule, and wherein the interpolymer has between 25 and 45 weight percent vinylidene-monomer units.

- 48. The article of claim 36 in which (1) that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less, (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that article, and (3) those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram, and an extractables content not greater than about 20 weight percent, such that the components (a), (b) and (c) of the article, when tested in the SAP-Utilization Test with deionized water, have a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.
 - 49. The article of claim 36 wherein (1) the article comprises a film or sheet having a thickness between 10 and 3000 microns, and (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that film or sheet.
 - 50. The article of claim 36 wherein (1) the article comprises at least one fiber having a cross-sectional thickness less than about 200 microns, and (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times that cross-sectional thickness.
 - 51. The article of claim 36 in the form of a foam.
 - 52. An article having a thickness, comprising:

5

15

20

25

- (a) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles, the size of those absorbent particles being sufficiently small to pass through a 150-micron sieve; and
- (b) between 30 and 80 weight percent of at least one matrix-polymer in which those absorbent particles are at least partially embedded so as to initially constrain those absorbent particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those absorbent particles from the matrix-polymer when those absorbent particles are swollen by contact with fluid, and
- (c) 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid, and

which components (a), (b) and (c) (when tested in the SAP-Utilization Test with deionized water) have a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.

53. The article of claim 52 in which those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that article.

5

10

15

20

25

- 54. The article of claim 52 in which those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram.
- 55. The article of claim 52 in which those absorbent particles have a content of extractable polymers less than about 20 weight percent (based upon the dry weight of the absorbent particles).
- 56. The article of claim 52 in which that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less.
- 57. The article of claim 52 in which that at least one matrix-polymer is one or more elastic polymers selected from the group consisting of an ethylene-based polymer or interpolymer, a propylene-based polymer or interpolymer, ethylene-propylene-diene monomer (EPDM) polymers, styrene block copolymers, hydrogenated styrene block copolymers, and blends of any one or more of the foregoing polymers or interpolymers.
- 58. The article of claim 52 in which that at least one matrix-polymer comprises one or more ethylene-based interpolymers formed by inter-polymerization of ethylene with one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule.
- 59. The article of claim 58 in which the at least one matrix-polymer comprises at least one homogeneous, substantially linear interpolymer of ethylene with at least one alphaolefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³, and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.
- 60. The article of claim 58 in which the at least one matrix-polymer comprises at least one homogeneous, linear interpolymer of ethylene with at least one alpha-olefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³ and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.

61. The article of claim 52 in which that at least one matrix-polymer comprises one or more propylene-based interpolymers formed by inter-polymerization of propylene with one or more comonomers selected from the group consisting of ethylene and alpha-olefin comonomers having between 4 and 20 carbon atoms per molecule.

5

10

15

20

25

- 62. The article of claim 61 in which that at least one matrix-polymer comprises at least one elastic, isotactic polypropylene homopolymer or interpolymer characterized as having: a MFR (ASTM D-1238, 230° C./2.16 kg.) less than about 100 gm/10 minutes; 13C NMR peaks at 14.6 and 15.7 ppm, the peaks of about equal intensity; and a B-value in excess of about 1.3, and wherein the interpolymer has between 8 and 20 weight percent ethylene-monomer units.
- 63. The article of claim 52 in which that at least one matrix-polymer comprises at least one interpolymer formed by inter-polymerization of ethylene, a vinylidene aromatic comonomer, and optionally one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule, and wherein the interpolymer has between 25 and 45 weight percent vinylidene-monomer units.
- 64. The article of claim 52 in which (1) that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less, (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that article, and (3) those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram, and an extractables content not greater than about 20 weight percent, such that the components (a), (b) and (c) of the article (when tested in the SAP-Utilization Test with deionized water) have a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.
- 65. The article of claim 52 wherein (1) the article comprises a film, ribbon, strip, band, strip, or sheet having a thickness between 10 and 3000 microns, and (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that film or sheet.
- 66. The article of claim 52 wherein (1) the article comprises at least one fiber having a cross-sectional thickness less than about 200 microns, and (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times that cross-sectional thickness.

67. The article of claim 52 in the form of a foam.

5

10

15

20

25

- 68. An elastic, porous article prepared by the method of:
- (A) forming a non-molten film or sheet having a thickness between 5 and 8,000 microns, said film or sheet comprising:
 - (1) between 20 and 70 weight percent of a plurality of fluid-swellable absorbent particles; and
 - (2) between 30 and 80 weight percent of at least one elastic matrix-polymer in which the absorbent particles are at least partially embedded to form an interconnected network of those particles within the matrix-polymer so as to initially constrain the particles but, upon contact with a fluid that swells those particles, permit the release of at least a portion of those fluid-swollen absorbent particles from the matrix-polymer and exposure of other absorbent particles that are interconnected with the released particles, and
 - (3) 0 to 5 weight percent of one or more surfactants that enhance the wetting of the matrix-polymer surface and the SAP particles when contacted with a fluid; and
- (B) contacting said film or sheet with a fluid so as to cause the swelling and release of at least a portion of those absorbent particles from the matrix-polymer, thereby creating a plurality of pores in the elastic matrix-polymer.
- 69. The article of claim 68 in which (i) the thickness of the film or sheet is between 5 and 500 microns, and (ii) the absorbent particles are of a size that pass through a sieve having openings of 150 microns or less.
- 70. The article of claim 68 in which those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram.
- 71. The article of claim 68 in which those absorbent particles have a content of extractable polymers no greater than about 20 weight percent (based upon the dry weight of the absorbent particles).
- 72. The article of claim 68 in which that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less.
- 73. The article of claim 68 in which that at least one elastic matrix-polymer is selected from the group consisting of an ethylene-based polymer or interpolymer, a propylene-based polymer or interpolymer, ethylene-propylene-diene monomer (EPDM)

polymers, styrene block copolymers, hydrogenated styrene block copolymers, and blends of any one or more of the foregoing polymers or interpolymers.

74. The article of claim 68 in which that at least one elastic matrix-polymer comprises one or more ethylene-based interpolymers formed by inter-polymerization of ethylene with one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule.

5

10

15

20

25

- 75. The article of claim 68 in which the at least one elastic matrix-polymer comprises at least one homogeneous, substantially linear interpolymer of ethylene with at least one alpha-olefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³, and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.
- 76. The article of claim 75 in which the at least one elastic matrix-polymer comprises at least one homogeneous, linear interpolymer of ethylene with at least one alphaolefin comonomer having between 3 and 8 carbon atoms per molecule, which interpolymer has a density, as measured by ASTM D-792, less than about 0.885 gm/cm³ and a Melt Flow Rate, as measured by ASTM D-1238 (190° C./2.16 kg.), of less than about 50 gm/10 min.
- 77. The article of claim 68 in which that at least one elastic matrix-polymer comprises one or more propylene-based interpolymers formed by inter-polymerization of propylene with one or more comonomers selected from the group consisting of ethylene and alpha-olefin comonomers having between 4 and 20 carbon atoms per molecule.
- 78. The article of claim 77 in which that at least one elastic matrix-polymer comprises at least one elastic, isotactic polypropylene homopolymer or interpolymer characterized as having: a MFR (ASTM D-1238, 230° C./2.16 kg.) less than about 100 gm/10 minutes; 13C NMR peaks at 14.6 and 15.7 ppm, the peaks of about equal intensity; and a B-value in excess of about 1.3, and wherein the interpolymer has between 8 and 20 weight percent ethylene-monomer units.
- 79. The article of claim 68 in which that at least one matrix-polymer comprises at least one interpolymer formed by inter-polymerization of ethylene, a vinylidene aromatic comonomer, and optionally one or more alpha-olefin comonomers having between 3 and 20 carbon atoms per molecule, and wherein the interpolymer has between 25 and 45 weight percent vinylidene-monomer units.

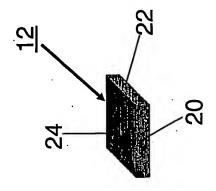
80. The article of claim 68 in which (1) that at least one matrix-polymer has a 2 percent Secant Modulus of about 60 MPa or less, (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that article, and (3) those absorbent particles have a modified centrifuge capacity (mCC) between 20 and 50 grams per gram, and an extractables content not greater than about 20 weight percent, such that the components (a), (b) and (c) of the article, when tested in the SAP-Utilization Test with deionized water, have a Max-SAP-Utilization Factor (A Factor) greater than about 60 percent, and an SAP-Utilization Rate (B Factor) greater than about 0.02 minutes⁻¹.

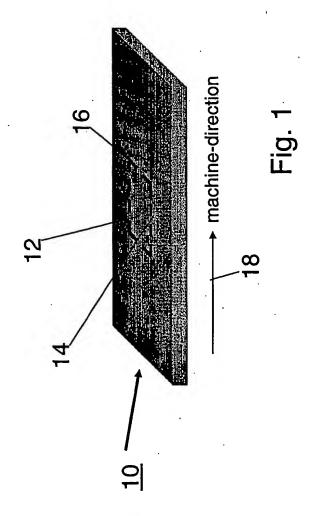
5

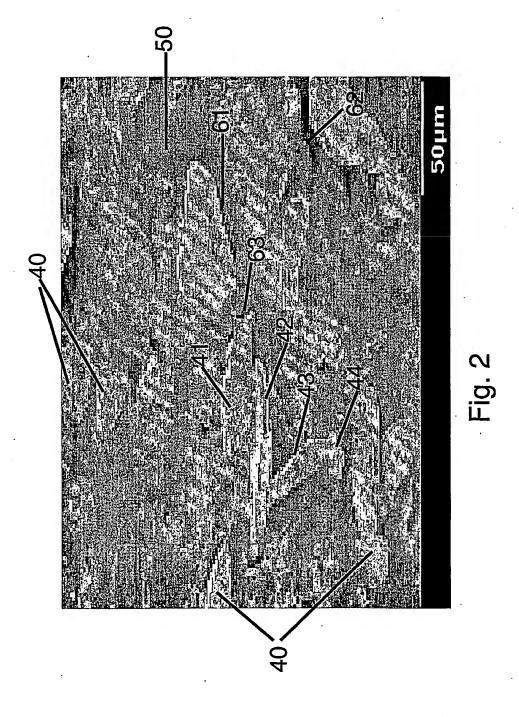
10

81. The article of claim 68 wherein (1) the article comprises a film or sheet having a thickness between 10 and 1000 microns, and (2) those absorbent particles are sufficiently small to pass through a sieve with openings that are no greater than about 0.8 times the thickness of that film or sheet.

PCT/US2004/012435

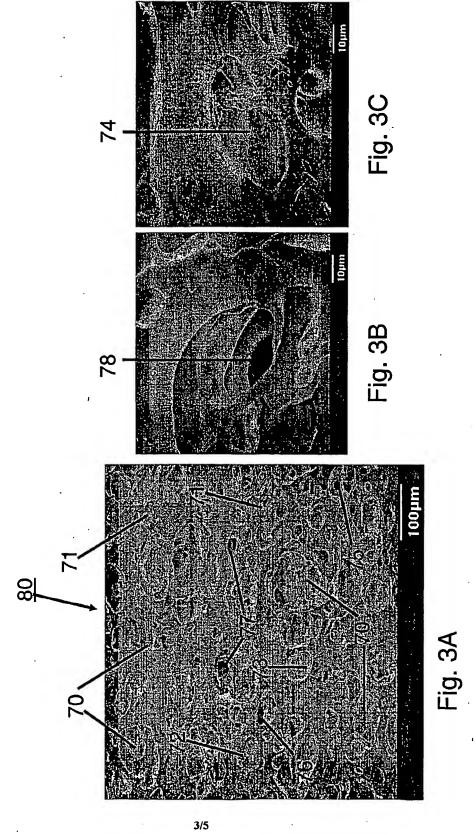


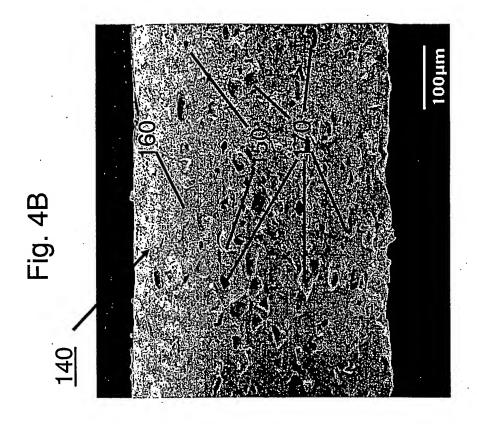




2/5

PCT/US2004/012435 WO 2004/096301





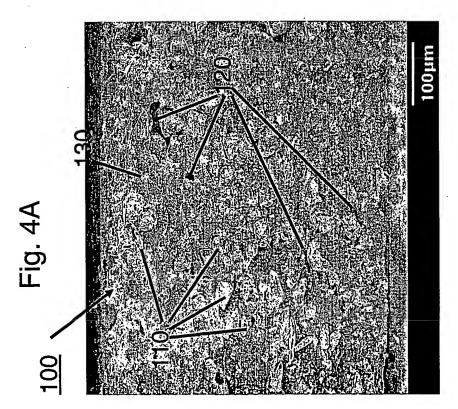


Fig. 5A 200

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

| Defects in the images include but are not limited to the items checked: | | | | | |
|---|--|--|--|--|--|
| □ BLACK BORDERS | | | | | |
| ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES | | | | | |
| ☐ FADED TEXT OR DRAWING | | | | | |
| BLURRED OR ILLEGIBLE TEXT OR DRAWING | | | | | |
| ☐ SKEWED/SLANTED IMAGES | | | | | |
| ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS | | | | | |
| GRAY SCALE DOCUMENTS | | | | | |
| LINES OR MARKS ON ORIGINAL DOCUMENT | | | | | |
| ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY | | | | | |
| □ other: | | | | | |

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.